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**SEDIMENTATION AND DIFFUSION
MEASUREMENTS ON CELLULOSE
AND CELLULOSE DERIVATIVES**

Inaugural Dissertation

by

NILS GRALÉN

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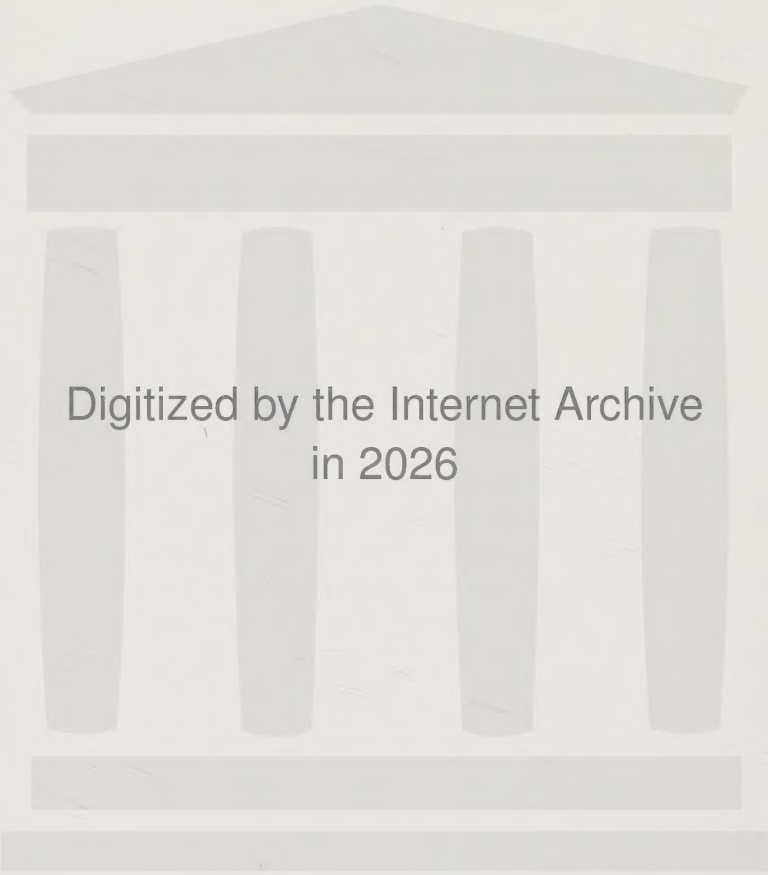
NILS GRALÉN

FIL. LIC., S.-N.

BY DUE PERMISSION OF THE PHILOSOPHICAL
FACULTY OF THE UNIVERSITY OF UPPSALA,
TO BE PUBLICLY DISCUSSED IN THE LECTURE
ROOM OF THE CHEMICAL INSTITUTE, ON APRIL
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Preface.

The present work has been carried out at the Institute of Physical Chemistry of the University of Uppsala in the course of the years 1940—1943.

To the head of the Institute, Professor The Svedberg, I desire to express my heart-felt gratitude. He introduced me to scientific physico-chemical research, and has been an encouraging and stimulating teacher. He created the possibilities for the execution of this investigation, and has shown a never-failing interest in my work. I am also grateful for his personal friendship.

I am indebted also to my colleagues at the Institute for valuable discussions and helpful advice.

The expenses incurred in connection with this work were defrayed in part by grants from the Royal Swedish Institute for Engineering Research, the Rockefeller Foundation, and the Wallenberg Foundation.

The investigations of technical celluloses and cellulose derivatives have been financially supported by Mo och Domsjö A.-B., A.-B. Svenskt Konstsilke, A.-B. Bofors Nobelkrut, Nitroglycerin A.-B., and A.-B. Express-Dynamit. I wish to acknowledge my indebtedness for the fruitful cooperation with the industrial concerns mentioned.

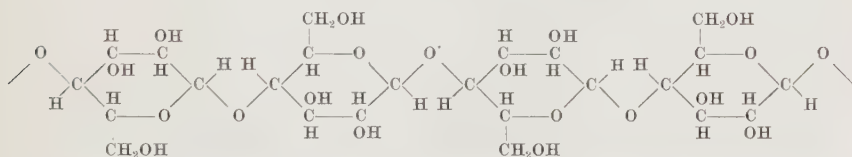
From a linguistic point of view, this paper has been revised by Mr. Grenville Grove, and the expense of this revision has been defrayed by a grant made by the British Council.

Uppsala, January 1944.

Nils Gralén.

Introduction.

The investigation of cellulose has proceeded on both a purely chemical and a physico-chemical basis. The chemical constitution of cellulose was long a central problem of cellulose chemistry. Willstätter and Zechmeister showed as far back as 1913 [100] that pure cellulose, $(C_6H_{10}O_5)_n$, yields on hydrolysis only glucose and is consequently built up exclusively of anhydro-glucose units. By the studies of several investigators (Haworth [15], Freudenberg [7], Irvine and Hirst [28], and others) the nature of the linkage between the glucose units was cleared up, and Haworth [14, 15] advanced the cellulose formula of to-day. According to that formula the glucose units are linked into chains by β -glucosidic bonds between the carbon atoms 1 and 4:



The knowledge of cellulose structure has been considerably extended by the use of physico-chemical methods. X-ray analysis (Sponsler and Dore [76], Meyer and Mark [49]) showed that cellulose is crystalline, at least in small areas. The crystal unit of cellulose, according to Meyer and Misch [50, 51], is reproduced in Fig. 1. It contains four glucose units. The glucose rings are chained to each other, and each glucose residue is turned 180° round the chain axis relatively to the following one. The glucose chains lie parallel or antiparallel, and the long cellulose molecules pass through several crystal units.

The known facts of the structure of the cellulose fibre and the theories that have been advanced on the subject (fibrils, fringe micells and so on) will not be discussed here. Reviews

have been given by Marsh and Wood [48], p. 120—132, Götze [10], p. 46—63, and others.

The problem of the size of the cellulose molecule has always attracted great interest, and much study has been devoted to the subject. There are various methods of determining the molecular weights, reviews of which are given by Ulmann [97], Marsh and Wood [48], p. 61—74, and others. Only the more noteworthy methods need be mentioned here. The end group method was elaborated especially by Haworth and Machemer [16, 17], and by

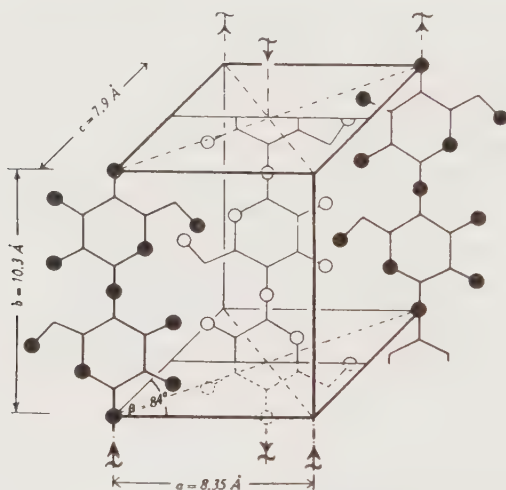


Fig. 1. The crystal unit of cellulose. (Meyer and Misch [50, 51].)

Hess and Neumann [23, 56]. The osmotic pressure method has hitherto not been used for cellulose itself, but only for its derivatives, esters and ethers, which are soluble in ordinary solvents. The viscosity method, introduced by Staudinger [81, 87], owing to its relative simplicity, has been very widely adopted, especially in technical investigations. Finally, mention should be made also of the ultracentrifuge method (Svedberg [91]). It has been used for cellulose and its derivatives by Stamm [77, 78], Kraemer [33, 34, 35, 38], Signer [73, 74], Mosimann [54, 55], and others.

All these methods have shown differences in the size of the molecules in different cellulose preparations. The native fibre celluloses, which occur in a free state in nature, e.g. cotton and ramie, have the highest molecular weights. Wood and straw

celluloses, which have been isolated from their native state by chemical agents, have smaller molecules. Even gentle chemical treatments entail a disintegration of the cellulose molecule, which is very sensitive to oxidation, hydrolysis, acetolysis, etc. The esterification and etherification of cellulose necessitate the use of highly acid or alkaline mediums and will usually break down the molecule into smaller units. According to Staudinger, nitration [86] and acetylation [85] can be performed without diminishing the molecule, provided that special precautions are taken.

The molecules of a given cellulose are not uniform in size. They form a polydisperse system. Staudinger [79] calls this system "polymerically uniform" (*polymereinheitlich*), as the molecules differ only in degree of polymerization. Schulz [67—70] and others have tried to determine the polydispersity by fractionating the system. A direct analysis of the polydispersity without fractionation can be made by means of the ultracentrifuge (Lansing and Kraemer [37, 46], Mosimann [55]). This subject will be further discussed later on.

It should be mentioned that the macromolecular structure of cellulose and its state in solution have been very extensively, and even hotly, discussed in the course of the last twenty years. In this paper the assumption has been made from the outset that the cellulose molecule has a molecular chain structure with exclusively primary valences, and that cellulose and its derivatives in dilute solutions are molecularly dispersed. This view is nowadays almost universally accepted.

This paper is intended to give an account of the sedimentation and diffusion behaviour of cellulose and some of its derivatives, namely two esters, cellulose nitrate (nitrocellulose) and the sodium salt of cellulose xanthate, and one ether, the sodium salt of cellulose glycollic acid, also named sodium cellulose glycollate. In connection with this study, some theoretical questions regarding the sedimentation and diffusion of thread-like molecules will also be discussed. Most of the experimental results are derived from researches made on behalf of some Swedish makers of cellulose, nitrocellulose and rayon.

Some preliminary results have previously been published (Grälén [11], Grälén and Svedberg [12]), and Svedberg has referred to some of them in a lecture [92].

CHAPTER I.

Sedimentation.

1. Method.

For the determination of the sedimentation velocity, Svedberg's oil turbine ultracentrifuge has been employed. A detailed description of the ultracentrifuge methods has been given by Svedberg and Pedersen in their monograph on the subject [91]. Merely a short review need therefore be given here.

The solution to be examined is put into a cell with quartz windows. The cell is fixed in a steel rotor and exposed to high centrifugal fields by rotation. For cellulose and cellulose derivatives centrifugal forces of 175 000 to 350 000 times gravity, obtained at the rate of 50 000 to 70 000 revolutions per minute, have been employed. The dissolved molecules will settle in the solution towards the periphery of the rotor under the influence of these high stresses. The boundary between sedimenting substance and pure solvent is observed through the cell windows by means of the scale method of Lamm [42—44]. This method is based upon the refractive properties of the solution. A scale with lines perpendicular to the direction of sedimentation is photographed through the cell. At the sedimenting boundary there is a concentration gradient and consequently a refractive index gradient, and the light beams will be bent. The scale lines therefore will appear to be shifted out of their original place on the photographic plate. The displacement, Z , is

$$Z = G a b \frac{dn}{dx}. \quad (1)$$

Here G is the photographic enlargement, a is the cell length in the direction of the light beam, b is the distance between the scale and the middle of the cell, and $\frac{dn}{dx}$ is the refractive index

gradient. The refractive index increment $\frac{dn}{dc}$ (where c is the concentration) may as a rule be regarded as a constant, whence Z will be proportional to the concentration derivative in the cell. By integration of the curve $Z(x)$ the concentration is obtained.

Every sedimenting boundary will be represented as a peak of the curve. From the position of the peak at different times the sedimentation velocity can be calculated. It will be given as sedimentation constant, s , calculated from the equation

$$s = \frac{dx}{dt} \frac{1}{\omega^2 x}, \quad (2)$$

where t is the time, ω the angular velocity and x the distance from the centre of rotation. It is corrected to 20° C., the density and viscosity changes of the solvent being taken into consideration. In the following it will always be given as the corrected value. The unit is one "Svedberg" ($1 S = 10^{-13}$ cm./sec. dyne).

If a diffusion measurement is added to the sedimentation analysis, the molecular weight of the material can be calculated by Svedberg's formula

$$M = \frac{R T s}{D(1 - V\rho)}. \quad (3)$$

R is the gas constant, T the temperature in Kelvin degrees, D the diffusion constant, V the partial specific volume of the solute and ρ the density of the solution.

2. The Sedimentation of Filamentous Molecules.

All substances dealt with in this work have molecules of an elongated, thread-like shape. The sedimentation of compact spherical molecules has been treated theoretically. The fundamental formula is that of Stokes

$$f_0 = 6\pi\eta Nr, \quad (4)$$

where f_0 is the molar frictional coefficient, which is related to the sedimentation constant by the formula

$$f_0 = \frac{M(1 - V\rho)}{s}. \quad (5)$$

N is Avogadro's number, η the viscosity of the medium and r the radius of the particle. An asymmetric particle of the same weight and density offers stronger resistance to displacement in the solution, the frictional coefficient f being greater than f_0 , and the sedimentation constant will be consequently smaller. The ratio f/f_0 can even be used as a measure of the asymmetry of the molecules.

The frictional resistance, however, will not be determined only by the shape of the single molecule, but is also influenced by the surrounding large molecules in the solution. The higher the concentration of the solution, the greater will f be, and s correspondingly smaller. For spherical molecules Burgers [3] has made a theoretical investigation of this effect. For filamentous molecules the possibility of mutual influence is increased by the enlargement of the surface of the particles. The dependence of the sedimentation constant on the concentration is therefore much more marked than in the case of spherical molecules. Unfortunately, the theoretical treatment has not yet been elaborated. For practical purposes (molecular weight determination) it is essential to know the sedimentation constant at infinite dilution. In default of a theory, a series of experiments at different concentrations must be carried out and an extrapolation made. The dependence on the concentration is so marked, especially with the thread-like molecules of high molecular weights, that this extrapolation presents great difficulties. Moreover, $\frac{ds}{dc}$ is greatest at the smallest concentrations, and the accuracy of the experiment diminishes rapidly on dilution. In earlier publications the extrapolation was carried out graphically from the curve $s(c)$ (Kraemer [38], Signer [72—74], Mosimann [54], and others). It has been ascertained by experience that s is linearly dependent on the product $s \cdot c$, at any rate with small concentrations, and this fact simplifies the extrapolation procedure. The s, c -function thus should obey the formula

$$s = \frac{s_0}{1 + kc}, \quad (6)$$

where s_0 is the sedimentation constant at zero concentration, and k is a constant. An expression of the same form as (6) was

theoretically found by Burgers to be valid for spherical molecules. The constant k , however, is of a different order of magnitude.

The boundary between the sedimenting substance and the solvent will be affected by the dependence of the sedimentation velocity on the concentration. The polydispersity of cellulose materials should always lead one to expect the boundary to be blurred, as molecules of different sizes will sediment at different rates. The largest and most rapidly sedimenting molecules will thus get into a region of higher concentration, so that their speed will be reduced. The smaller molecules, on the other hand, if they should settle rearwards, will get into a more dilute medium and thus be accelerated. The general effect will be a sharpening of the boundary. At higher concentrations this sharpening may become so pronounced that the observed scale line displacement on the photograph will be limited to a few or even a single line (the distance between the scale lines = 0.135 mm.). As the area under the curve is proportional to the concentration and thus given *a priori*, the height of the curve, i. e. the maximum line displacement, will be very great. The direction of the light beams through the boundary will sometimes be deflected to such an extent that they miss the objective, so that a "Schliere" is produced on the photographic plate.

It will be of interest to study the shape of the sedimentation curve in greater detail. In the following discussion the diffusion of the molecules will not be taken into consideration. In the case of filamentous molecules this is justifiable, in view of their very slight diffusion. It is quite generally assumed that the polydispersity of the material causes a distribution of the sedimentation constants (at infinite dilution) expressed by the equation

$$\frac{dc}{ds_0} = f(s_0). \quad (7)$$

The formula for the calculation of the sedimentation constant (2) can be approximately given as

$$s = \frac{x - x_0}{(t - t_0) \omega^2 x_m}, \quad (8)$$

where x_0 is the position of the meniscus of the solution, $t - t_0$ is the time from the beginning of the sedimentation and x_m is

an average for x during the time of sedimentation. x_m is much larger than $x - x_0$, and the variation of x_m over a sedimentation curve will as a rule be less than 5 per cent. If it is considered as a constant, we find at a given point of time

$$s = \text{const. } (x - x_0) \quad (9 \text{ a})$$

and

$$d s = \text{const. } d x. \quad (9 \text{ b})$$

As $\frac{d n}{d c}$ may be regarded as a constant, and if the concentration changes owing to the sedimentation in a sector-shaped cell are not taken into consideration, we get

$$\frac{d n}{d x} = \text{const. } \frac{d c}{d s}. \quad (9 \text{ c})$$

If the coordinate units are suitably changed, the experimental sedimentation curve will thus approximately give the distribution function

$$\frac{d c}{d s} = f_c(s). \quad (10)$$

The index c should signify that the function depends on the concentration. If this dependence could be eliminated, the function (7) would be obtained.

For the systems under investigation here, the function (7) as a rule has only one maximum, which is obtained for $s_0 = s_1$, and for very small or very large values of s_0 , $\frac{d c}{d s_0}$ will be $= 0$. The discussion in the remainder of this section will be restricted to this form of the function. It will at any rate be assumed that any accessory maxima are small.

If the dependence of the sedimentation constant on the concentration is given by (6) and s is substituted for s_0 in (7), we obtain

$$\frac{d c}{d s} = \frac{(1 + k c) \cdot f(s_0)}{1 - k s \cdot f(s_0)} \quad (11)$$

or

$$\frac{d c}{d s} = \frac{(1 + k c)^2 \cdot f(s_0)}{1 + k [c - s_0 \cdot f(s_0)]}. \quad (12)$$

Here k has been treated as a constant. It certainly varies with the molecular size (cf. p. 100), but this variation will not appreciably affect the following reasoning.

The expression $c - s_0 f(s_0)$ in the denominator of (12) is negative when s_0 is small. This can be shown by a simple geometric representation. The product $s_0 f(s_0)$ is represented by the area of the rectangle R in Fig. 2, but c is merely the hatched part of it. When s_0 is larger than s_1 , c will increase more rapidly

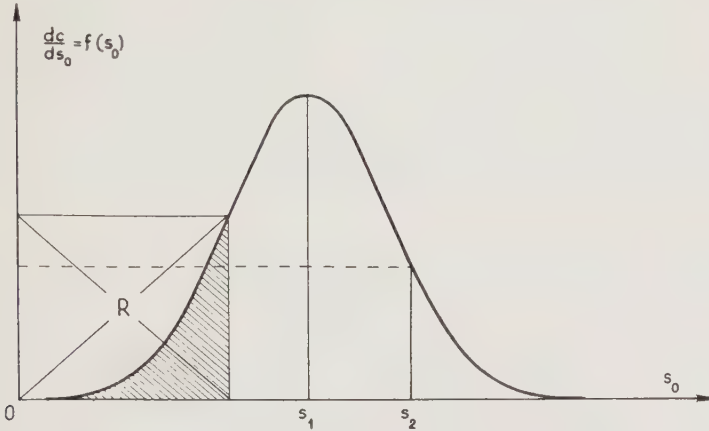


Fig. 2. To the theory of the shape of the sedimentation curve.

than $s_0 f(s_0)$ with increasing s_0 . For still larger s_0 , $s_0 f(s_0)$ will decrease, and at a given value s_2 we will get $c = s_0 f(s_0)$. For very high values of s_0 , $s_0 f(s_0)$ approaches zero. Thus for small s_0 we get

$$\frac{dc}{ds} > (1 + kc)^2 f(s_0)$$

and for large values of s_0

$$\frac{dc}{ds} = (1 + kc) f(s_0).$$

In any case $\frac{dc}{ds}$ is larger than $f(s_0) = \frac{dc}{ds_0}$.

A second derivation of (12) gives

$$\frac{d^2 c}{ds^2} = \left\{ \frac{1 + kc}{1 + k(c - s_0 f)} \right\}^3 \{ 2k[1 + k(c - s_0 f)]f^2 + (1 + kc) \cdot f' \}, \quad (13)$$

where f' denotes $\frac{df}{ds_0} = \frac{d^2c}{ds_0^2}$. If $f' = 0$, which is valid for the maximum point $s_0 = s_1$ of the function (7), $\frac{d^2c}{ds^2}$ will be positive. The function $\frac{dc}{ds}$ is consequently rising for $s_0 = s_1$, and the maximum of $\frac{dc}{ds}$ is obtained for a value of $s_0 > s_1$. The difference will be more marked, the larger the concentration. The calculated value of s , taken from the apex of the peak, thus does not correspond to the same molecules in the experiments at different concentrations. The effect of the displacement of the maximum is that the part of the curve which falls towards higher sedimentation constants will be steeper at higher total concentrations. This effect has been verified by the experiment.

3. Determination of Polydispersity from Sedimentation Experiments.

Svedberg and Rinde [89, 63] have shown how it is possible to determine the particle weight distribution function from the sedimentation diagram, if the particles sediment free from each other. Rinde [63] also elaborated methods for the case of sedimentation equilibrium, but they were somewhat laborious in application. Sedimentation equilibrium was afterwards treated theoretically by Lansing and Kraemer [46]. Part of their reasoning will be reviewed here, as being of interest for the following discussion.

For a polydisperse system various averages of molecular weights can be given. By osmotic measurements a *number average* is obtained:

$$M_n = \frac{\sum c_i}{\sum c_i/M_i} = \frac{\sum n_i M_i}{\sum n_i}. \quad (14)$$

M_i , c_i and n_i denote molecular weight, concentration and number of particles of the i -th component in the polydisperse mixture. By the sedimentation equilibrium method a *weight average* is obtained:

$$M_w = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}. \quad (15)$$

This method also affords the possibility of calculating a so-called *Z-average*, which is defined by the following equation:

$$M_Z = \frac{\sum c_i M_i^2}{\sum c_i M_i} = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}. \quad (16)$$

For a uniform (monodisperse) system all these three averages are equal, but in case of polydispersity

$$M_Z > M_w > M_n \quad (17)$$

and the ratio between two of these values gives a measure of the degree of polydispersity.

Lansing and Kraemer developed their theory further by arbitrarily assuming a logarithmic distribution of the molecular weights, according to the formula

$$dw = \frac{W}{M_n \beta \sqrt{\pi}} \cdot e^{-y^2} dy, \quad (18)$$

where

$$y = \frac{1}{\beta} \log (M/M_0).$$

Here W is the total weight, dw is the weight of the molecules of a molecular weight between M and $M + dM$. W and dw may be replaced by c (total concentration) and dc . M_0 is the molecular weight at the maximum of the weight distribution curve. The coefficient β is a measure of the spread of the distribution and is termed "non-uniformity coefficient". For uniform substances β is 0. For polydisperse systems with the above distribution the relation

$$M_Z/M_w = M_w/M_n = e^{\beta^2/2} \quad (19)$$

is valid. From a sedimentation equilibrium experiment M_Z and M_w and thus β may be calculated. Even if the distribution function (18) is not valid, a calculation of β by these formulas will be of interest, as it will give a possibility of comparison between different polydisperse systems.

From the sedimentation velocity experiments it will not be possible directly to determine the molecular weight distribution, but it should be possible to determine the distribution of the

sedimentation constants in accordance with the reasoning of section 2 of this chapter. For filamentous molecules this determination must always be made by extrapolations.

As a relative measure of the polydispersity from sedimentation experiments, the width of the sedimentation curve may be adopted. The diffusion can be neglected, as, in the case of filamentous molecules, it never involves errors larger than two or three per cent. The sedimentation curve may assume various shapes, whence the quotient between area (A) and maximum height (H) was adopted as a general measure of the width (B) of the curve:

$$B = \frac{A}{H}. \quad (20)$$

In determining the area and height there are always difficulties in drawing the base line of the curve. It can rarely be determined with sufficient accuracy by measuring the index lines on the photographic plates. It has been found that on drawing the apparently required line at a venture, the area will often be smaller than the one that could be calculated from the analytical concentration. This effect occurs especially in the case of late exposures and low concentrations, where the curve is low and wide, the ends asymptotically approaching to the base line. For this reason, the proper area was first calculated from the analytical concentration and the known experimental constants, and the base line was drawn so that the correct area was obtained. This could as a rule be done without violating the experimental results. It is obviously correct to assume a constant concentration throughout the experiment, and this condition is not fulfilled by the arbitrary drawing of the base line. The height is taken as the distance between the maximum point and the calculated base line.

As the experiments show, B varies linearly with x , and the derivative $\frac{dB}{dx}$ varies with the total concentration of the solution.

From a diagram with $\frac{dB}{dx}$ as ordinate and c as abscissa, an extrapolation to $c=0$ may be made. In this way the curve width for free sedimentation is obtained. The extrapolation has been

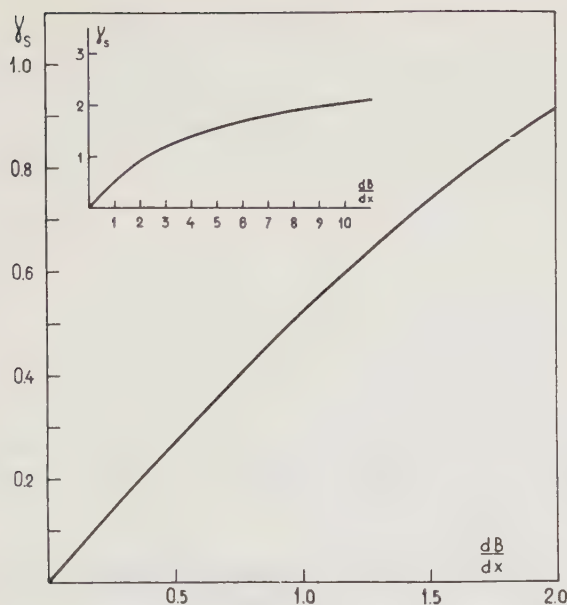


Fig. 3. The relation between $\left(\frac{dB}{dx}\right)_{c=0}$ and γ_s .

facilitated by the fact that $\frac{dB}{dx}$ is approximately a linear function of the quantity $\frac{c}{1 + kc}$, where k has the same value as in (6).

Owing to experimental inaccuracies with small concentrations, the procedure does not give very exact results, but it is nevertheless very useful for comparative investigations.

It is of interest to compare the quantity $\left(\frac{dB}{dx}\right)_{c=0}$ with other measures of polydispersity. In analogy with Lansing and Kraemer's procedure for the molecular weights, a logarithmic distribution of sedimentation constants could be arbitrarily assumed:

$$dc = K_s \cdot e^{-y^2} ds_0 \quad (21)$$

where

$$y = \frac{1}{\gamma_s} \log(s_0/s_1),$$

K_s is a constant, the maximum height of the distribution curve, and γ_s is the distribution coefficient for the sedimentation constants.

There must be a certain relation between γ_s and the non-uniformity coefficient β , and this relation corresponds to the relation between molecular weight and sedimentation constant. In Chapter IV this relation will be further discussed.

If the equations (9) are taken into consideration, we obtain for $\left(\frac{dB}{dx}\right)_{c=0}$

$$\left(\frac{dB}{dx}\right)_{c=0} = \frac{\int_0^{\infty} \frac{dc}{ds_0} ds_0}{\left(\frac{dc}{ds_0}\right)_{\max.} \cdot N_1} = \gamma_s \cdot e^{\gamma_s^2/4} \cdot \pi. \quad (22)$$

The relation between $\left(\frac{dB}{dx}\right)_{c=0}$ and γ_s is illustrated in Fig. 3.

4. Reagents and Apparatus.

Sedimentation experiments have been performed with the following solutions:

Cellulose in copper oxide ammonia (Schweizer's reagent, [71]), abbreviated cuprammonium;

Cellulose nitrate in acetone;

Sodium cellulose xanthate in alkaline water solutions;

Sodium cellulose glycollate in water.

Cuprammonium was manufactured according to the method of Lottermoser and Wultsch [47]. By precipitating a copper sulphate solution with ammonia a basic copper sulphate was obtained, which after careful washing was dissolved in concentrated ammonia. For the purpose of stabilization, 1 g. glucose per litre was added. The copper content was adjusted to 13 g. per litre and the ammonia (NH_3) content to 200 g. per litre. In different preparations, minor, insignificant variations occurred. Table 1 gives the analyses, the densities and the viscosities of the preparations used.

The cuprammonium solutions of cellulose are sensitive to oxygen and to light (Gibson [8]). In order to avoid the influence of oxygen, all the operations were made in a nitrogen atmosphere. Light could not be completely excluded, as it is necessary to use relatively intense violet light (mercury lamp, 436 m μ) in

Table 1. *Properties of cuprammonium preparations.*

Prep. No.	g. Cu per litre	g. NH_3 per litre	Density, 20°	Viscosity, 20°, rel. water
1	13.0	190	0.9448	1.344
2	12.5	196	0.9427	1.338
3	13.0	201	0.9428	1.351
4	12.3	190	—	1.331
5	13.4	199	—	1.367
6	12.9	199	—	1.357
7	12.7	199	—	1.373
8	12.9	200	—	1.347

making sedimentation and diffusion measurements. As far as possible, all the flasks were enclosed in black covers, and all the apparatus were placed in a room where only medium incandescent lamps (no sunlight) were used for illumination. Ultraviolet light was always excluded by glass filters between light source and solution, and the exposure times were the shortest possible.

Nitrogen was taken from bombs and purified. Pyrogallol and chromous chloride in washing flasks were at first used for purification (Lottermoser and Wultsch [47]). Afterwards, nitrogen was led over heated copper. This method of purification was formerly considered inadequate (Kautsky and Thiele [32]). Subsequent investigations (Meyer [53]) have, however, shown that the oxygen pressure of copper oxide is not disturbing if there are at least 30 cm. of unoxidized copper after the oxidized layer in the direction of the current, and if the velocity is not more than 250 cc. per minute with a tube diameter of 17 mm. These precautions were duly observed. No differences in the results have been noticed in using the different methods of nitrogen purification.

For the dissolution of the cellulose and the transfer of the solutions into various receptacles (centrifuge cell, diffusion cell, viscometer), a special arrangement was designed. Arrangements for viscosity measurements in nitrogen atmosphere have been described by Lottermoser and Wultsch [47], Heuser and Green [25], Zimmermann [102], and others, and have been partly adopted here.

Fig. 4 shows the dissolving arrangement. The flask *E* (capacity 7 litres) is the cuprammonium storage. Above the solution it contains pure nitrogen. *F* is a measuring flask (100 or 125 ml.)

which serves as a dissolving vessel. Fig. 5 is a photograph of *F*. The whole arrangement is made mainly of glass, the necessary connections consisting of rubber vacuum ligature.

The detailed manipulation of the arrangement will not be described here, being in conformity with the above-mentioned descriptions, to which the reader is referred. The cellulose is weighed into the flask *F*. *F* is alternately evacuated and filled with nitrogen. If in this way a mole of a gas should be replaced

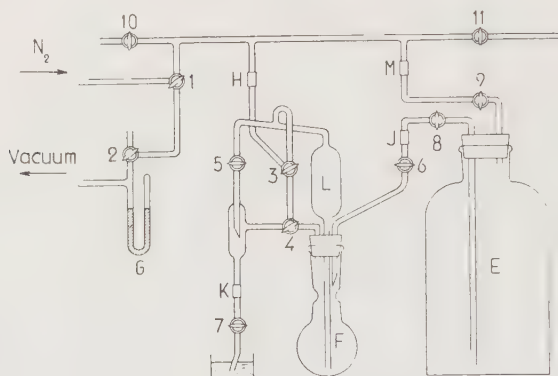


Fig. 4. Arrangement for the dissolution of cellulose in cuprammonium in a nitrogen atmosphere.

E is the cuprammonium storage flask, *F* the dissolver flask, *L* a bulb for mixing of the solution, *H*, *J*, *K*, and *M* rubber vacuum ligature connections, *G* a manometer, 1—4 three-way cocks, 5—11 ordinary cocks.

by that of another gas, so that only a single molecule of the first one is left, the following equation will be theoretically valid

$$\left(\frac{p_1}{p_2}\right)^n = \frac{1}{N},$$

where p_1 represents the pressure reached on evacuation and p_2 the pressure of the inflowing gas, N is Avogadro's number and n the necessary number of evacuations. For $p_1 = 20$ and $p_2 = 760$ mm. Hg we get $n = 15$. It should, of course, be borne in mind that the diminution of the gas diffusion by the use of narrow tubes and the adhesion of oxygen to glass and cellulose will affect the value of this calculation. For practical purposes, however, 15 evacuations were considered sufficient for replacing the air by pure nitrogen; and the oxygen residue will certainly be very small.

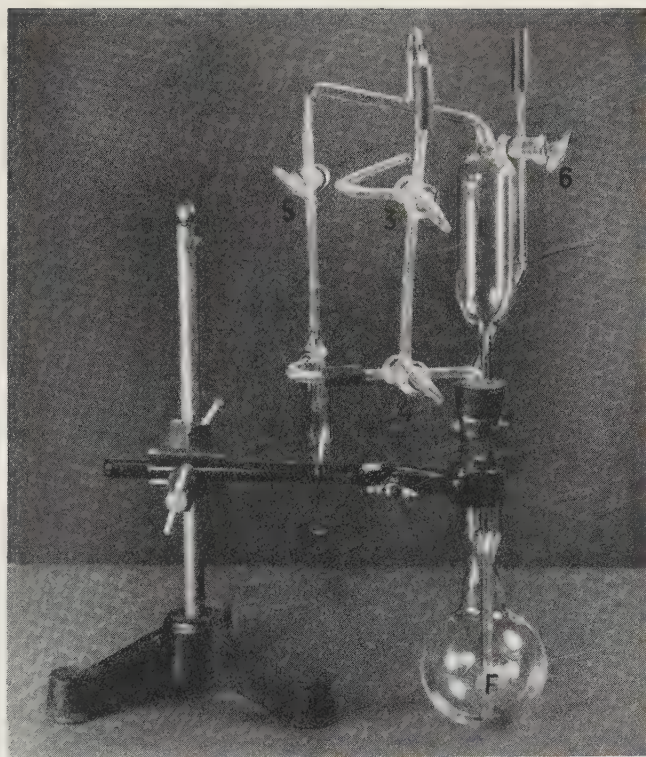


Fig. 5. Flask for dissolution of cellulose.
For explanation see text to Fig. 4.

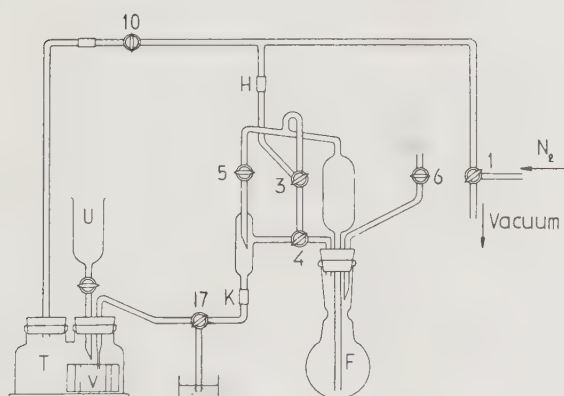


Fig. 6. Arrangement for the filling of a centrifuge cell in a nitrogen atmosphere.
For explanation see Fig. 4 and the text.

When the whole system is filled with nitrogen, cuprammonium is pressed into *F* up to the mark. *F* is shut off and removed. For the dissolution of the cellulose, the flask is rotated excentrically with inclined axis, as a rule over night.

The filling of a centrifuge cell is illustrated in Fig. 6. The cell *V* is placed under a glass bell *T*. The drop funnel *U* contains liquid paraffin and its cock is filled and lubricated with liquid paraffin. The flask *F* is shut off during the process of filling the bell with nitrogen, whereupon the solution is pressed through the bulb *L* and the tubes to the cell.

The first part of the solution, the composition of which may not be quite the same as that of the bulk of the solution, can be discharged through the cock 17. When the cell is filled, a paraffin layer is poured on top of the solution. On fixing the cell in the centrifuge rotor, it must always be reversed. On this reversion the cuprammonium solution may come into contact with the air. In order to obviate this, the cell is provided with a duraluminium lid, which is put on in such a way that no air comes in between the lid and the liquid paraffin. The upper edges of the lid are cut off and in the grooves thus obtained, solid paraffin is melted.

The sector plate of the centrifuge cell is generally made of tufnol, an artificial resin reinforced with a narrow woven fabric. As this fabric is of a cellulosic material, tufnol could not be used for the cuprammonium solution. Ebonite was employed, instead, and it has worked well. The strength of this material, however, limits the possible centrifugal forces to about 200 000 *g*. and the experiments were made at 50 000 r. p. m., which is quite sufficient. As a packing material between the sector plate and the quartz windows, thin rubber (0.12 mm.) was employed. The length of the cell was 12 mm. in the direction of the light beam.

For the photographic observation, a mercury arc light of wave length 436 m μ was employed. The exposure time necessary for the plates ("Agfa Spektral blau") is only about 50 per cent more than for uncoloured solutions.

For the cellulose nitrate solutions in acetone a cell with a tufnol sector plate was employed. The packing was cellophane and the cell had a lid of duraluminium with a rubber support. It has been shown (Jullander, unpubl.) that the risk of convec-

tion currents in the cell for volatile liquids is best avoided by diminishing the speed. These solutions were as a rule run at 50 000 r.p.m. The light for exposures was 436 m μ Hg.

The alkaline xanthate solutions were examined in an ordinary water cell (tufnol with rubber packings). The crystalline quartz windows very well stand an alkalinity of even 6 % NaOH. The sedimentation constants of the molecules in these solutions were rather low, and they were run up to the limit capacity of the rotor (65 000 r.p.m., corresponding to 300 000 *g*). The yellow colour of the solution made it necessary to use the greenish yellow line of mercury light, 546 m μ , which was obtained with a "Wratten 77" filter. Plates were "Agfa Spektral gelb".

Sodium cellulose glycollate solutions were run in an ordinary water cell at the highest possible speed and exposed in violet light.

5. Materials Investigated, and Results of Sedimentation Measurements.

a. The Sedimentation of Cellulose in Cuprammonium.

Raw Georgia Cotton (strict middling) was taken directly from a bale. It seemed essential to examine the cellulose in as native a state as possible, without any intervention, and any purification was therefore avoided. On weighing out 0.3 g. in 100 ml., 91 per cent dissolved in cuprammonium. The undissolved residue may have consisted in impurities of non-cellulosic materials (cuticula, fat, ash). The sedimentation of cotton cellulose is illustrated in Table 2 and Fig. 7. In Fig. 7, *x* (distance from centre of rotation) is the abscissa, and as the ordinate $\frac{Z}{b \cdot c}$ is taken (for notation see above, p. 10). According to equation (1) we have

$$\frac{Z}{b \cdot c} = \frac{G \cdot a}{c} \cdot \frac{dn}{dc} \cdot \frac{dc}{dx},$$

and if *c* is considered constant (the sector effect being disregarded) integration gives

$$\int \frac{Z}{b \cdot c} dx = \frac{Ga}{c} \cdot \frac{dn}{dc} \int dc = Ga \cdot \frac{dn}{dc},$$

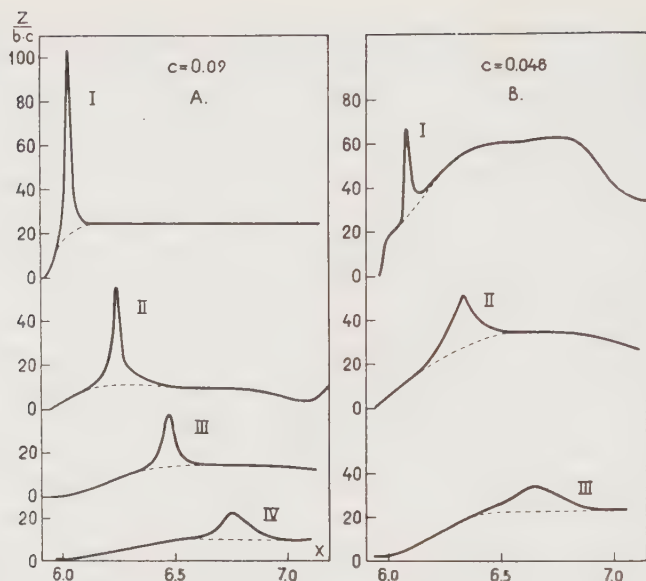


Fig. 7. Sedimentation curves of raw Georgia cotton cellulose in cuprammonium.
Abscissa: distance from centre of rotation (cm.).

Ordinate: $\frac{Z}{bc}$.

		t	x	B
A: $c = 0.09$	I	30 min.	6.014 cm.	0.04 cm.
	II	60 "	6.234 "	0.06 "
	III	100 "	6.472 "	0.09 "
	IV	140 "	6.752 "	0.16 "
B: $c = 0.046$	I	30 min.	6.075 cm.	0.05 cm.
	II	60 "	6.320 "	0.11 "
	III	100 "	6.635 "	0.21 "

i.e. a constant value. The area under the curve will thus be constant for different exposures and total concentrations, which will facilitate comparison. From Fig. 7 it can be seen how the width of the curve increases with dilution. At higher concentrations than those reported in the figure, "Schlieren" are obtained.

The base lines of the curves are somewhat distorted, especially at low cellulose concentrations, where large scale distances had to be used. This is due to differences in the experimental conditions between the actual run and the reference-scale run. Owing to the high amount of ammonia in the solution, very small experimental differences, which are unavoidable, cause large distortion effects (cf. Svedberg and Pedersen [91], p. 290).

Table 2 gives the sedimentation constants, as calculated from the apices of the peaks, as well as the products $s \cdot c$, where c is the total concentration in the experiment. The extrapolation of s to concentration 0 is illustrated in Fig. 8, which gives s as a function of c and of $s \cdot c$. From the theoretical exposition it is clear that this procedure of calculation and extrapolation is not quite cor-

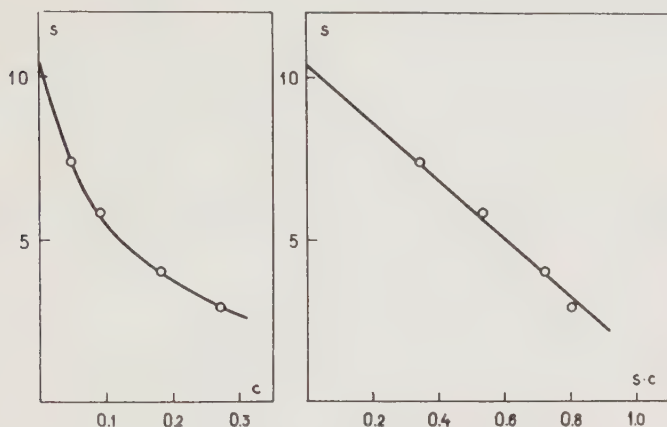


Fig. 8. The sedimentation constant of raw Georgia cotton cellulose as a function of the concentration c (to the left) and of the product $s \cdot c$ (to the right).

Table 2. *Raw Georgia cotton.*

c (g./100 ml.)	s	$s \cdot c$	$\frac{dB}{dx}$
0.27	2.9	0.80	0 (Schliere)
0.18	4.0	0.72	0 "
0.09	5.85	0.53	0.13
0.046	7.4	0.34	0.29
0	10.4	—	0.55
	$k = 9.0$		$\gamma_s = 0.31$

rect, firstly because the apex does not correspond to the same molecules for runs at different concentrations, and secondly because the s calculated from the apices does not correspond to the total concentration in the experiment. The s calculated is, however, an average for the various molecules in the mixture, and the errors involved diminish on dilution and disappear on extrapolation. For simplicity's sake, this procedure has always been adopted. The equation (6) may be applied to this procedure,

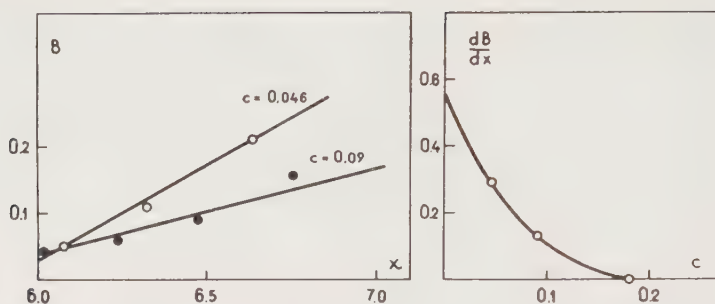


Fig. 9. B as a function of x , and $\frac{dB}{dx}$ as a function of c for the raw Georgia cotton cellulose.

though with due allowance for the inappropriateness involved, which cannot simply be avoided. For the special case of raw Georgia cotton, it gives $s_0 = 10.4$ and $k = 9.0$, if c is expressed in g. per 100 ml.

In Table 2 also $\frac{dB}{dx}$ at different concentrations is given. The measurement of $\frac{dB}{dx}$ is illustrated in Fig. 9, which gives B as a function of x for the experiments shown in Fig. 7, and also the extrapolation of $\frac{dB}{dx}$ to zero concentration. In the determination of the position of the base line the value of $dn/dc = 233 \cdot 10^{-5}$ has been used for all celluloses in cuprammonium (cf. p. 85).

Unbleached American cotton linters were also investigated without any preliminary treatment. They dissolved to 94 per cent in cuprammonium. The results of the sedimentation measurements are given in Table 3.

Table 3. *Unbleached American linters.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.38	2.85	1.09	0
0.195	4.75	0.93	0.05
0.095	6.7	0.64	0.15
0.047	7.9	0.37	0.23
0	10.3	—	0.36
	$k = 6.0$		$\gamma_s = 0.20$

The solution of concentration 0.095 g. per 100 ml. was centrifuged after storage for one, two, and three days, and the sedimentation constants obtained were 6.7, 6.2, and 5.5, respectively. The unbleached linters are thus affected by cuprammonium, probably depolymerized. Staudinger and Schweitzer [80] have found similar effects on viscosity measurements of this high-molecular, very susceptible cellulose. This depolymerization is probably due to the minute oxygen amounts which cannot be removed (cf. Golova and Nikolaeva [9]). All the other centrifugations, also of other celluloses, were performed about 24 hours after the commencement of the dissolution.

Bleached American cotton linters (probably bleached by hypochlorite) dissolved completely in cuprammonium. The following results were obtained:

Table 4. *Bleached American linters.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
1.05	1.24	1.30	0
0.99	1.39	1.38	0
0.52	2.06	1.07	0
0.34	2.6	0.88	0.03
0.20	3.5	0.70	0.15
0.105	4.7	0.49	0.36
0	7.2	—	0.89
	$k = 5.2$		$\gamma_s = 0.48$

The bleaching thus entailed a decrease of the sedimentation constant (and the molecular weight). The increase of the polydispersity is remarkable.

Linters were also *bleached* in the laboratory by means of *sodium chlorite* ("Textone", cf. Vincent and co-workers [5, 93], Wenzel [98], Jayme and Mo [29]). The treatment was made in the same way as for the holocellulose preparation from wood (cf. p. 34). The bleached material was completely soluble in cuprammonium. The sedimentation results are given in Table 5.

This bleaching method has obviously affected the sedimentation constant less than the former one.

Flax fibres were prepared in the laboratory from flax (Swedish "Konkurrentlin") in the ordinary way. The method of retting

Table 5. *Chlorite bleached linters.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	2.17	1.09	0
0.30	2.9	0.87	0
0.20	3.9	0.78	0.08
0.10	5.5	0.55	0.31
0.05	6.8	0.34	0.57
0	9.2	—	0.87
$k = 6.9$			$\gamma_s = 0.47$

Table 6. *Flax fibres.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.44	2.4	1.06	0
0.174	4.3	0.74	0
0.087	7.7	0.67	0.06
0.087	6.8	0.59	0.09
0.044	9.5	0.41	0.31
0.026	12.2	0.32	0.30
0	17.5	—	0.60
$k = 17$			$\gamma_s = 0.33$

adopted was that of water-retting at about 30° for a week, and after drying the fibres were mechanically purified. They were as to 87 % soluble in cuprammonium.

Flax fibres have yielded the highest sedimentation constants obtained.

Nettle fibres were in the same way extracted from common stinging nettles (*Urtica dioica* L.). Out of 0.3 g. weighed into 100 ml. cuprammonium, 80 % dissolved.

*Ramie fibres*¹ were soluble in cuprammonium to 81 %.

As pointed out in the introduction, the prepared wood celluloses have lower molecular weights than the native fibre celluloses (cf. Chapter IV). It was considered to be of interest to investigate also the wood celluloses in a more native state, with a view to a direct comparison between the celluloses from the two different sources. Cellulose, however, is very closely bound

¹ The author is indebted to Mr. Alex. Engblom, Chief Engineer, for supplying the ramie fibres.

Table 7. *Nettle fibres.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.24	4.0	0.97	0
0.16	5.7	0.91	0
0.08	7.7	0.61	0.13
0.04	10.1	0.40	0.29
0	14.0	—	0.54
	$k = 10$		$\gamma_s = 0.30$

Table 8. *Ramie fibres.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.24	3.3	0.79	0
0.16	4.6	0.74	0
0.08	6.5	0.52	0.21
0.04	7.9	0.32	0.40
0	10.8	—	0.71
	$k = 8.6$		$\gamma_s = 0.39$

to other constituents of the wood, namely lignin and hemi-cellulose, and it has never been found possible to isolate it without rupturing some of the cellulose chain bonds.

Attempts have previously been made to dissolve the cellulose of wood directly in a cellulose solvent, e.g. cuprammonium. Bergström and Cederquist[1] found that the amount dissolved depends on how finely divided the wood is. A wet grinding of the wood was found to be especially advantageous for the dissolving in cuprammonium. The said authors did not measure the molecular weights of their dissolved celluloses. Later experiments by Staudinger *et al.*[82, 83] and Hess *et al.*[24] have shown that grinding of cellulose entails a rather marked depolymerization.

The author's experiments concerning the extraction of cellulose from wood with cuprammonium were made in cooperation with Mr. Stig Berg, Engineer.

Spruce wood was finely divided in a mill (to about 60 mesh), extracted with acetone for 24 hours in a Soxhlet apparatus, and stirred with cold water for four days. After drying at room temperature, the wood was treated with cuprammonium in an

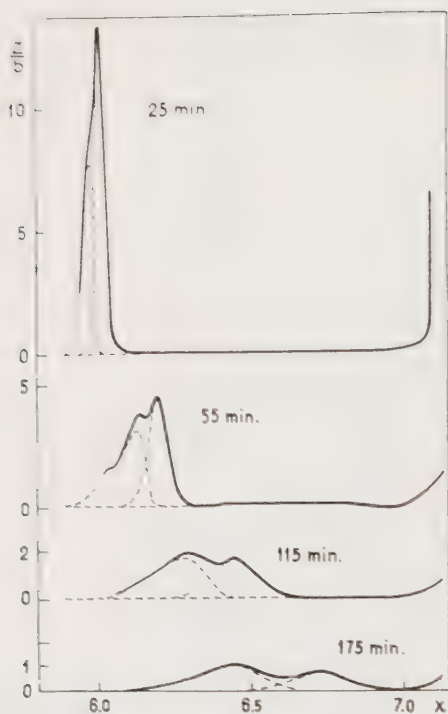


Fig. 10. Sedimentation diagrams of cuprammonium extract from wood.

ordinary dissolver flask in a nitrogen atmosphere for 24 hours. As a rule the proportion of wood was 2 g. per 100 ml. solvent.

The sedimentation diagram of the solution obtained is given in Fig. 10. It shows two peaks, corresponding to two molecular species. From the area under the curves the concentration can be determined. It was found that it corresponds in general to 5—10 per cent of the wood. The holocellulose content of wood should be about 70 per cent (cf. p. 34). The sedimentation constant of the slower component (to the left in the diagrams) is between 2.0 and 2.5, whereas that of the faster one varies appreciably,

according to the concentration dissolved. It was found to be 4.8, 5.0 and 6.9 in three different experiments, where the concentrations of the component were 0.13, 0.10, and 0.03 respectively, as calculated from the areas under the curves. These values correspond to a value of s_0 about 8.0.

The two peaks of the diagram presumably correspond to the hemicellulose and cellulose part of the wood (cf. the sedimentation investigation of holocellulose, p. 34 ff.). The third constituent of wood, lignin, is almost insoluble in cuprammonium (Freudenberg [6]). This interpretation is, of course, rather schematic. It is, for instance, quite possible that the observed components contain compounds of lignin and carbohydrates.

Grinding of the wood in a ball mill before treatment with cuprammonium did not change the configuration of the diagram.

The grinding was made in a dry state and at a low temperature (in liquid air).

If the wood was pretreated with 2 N HCl at room temperature for 24 hours, the amount dissolved in cuprammonium increased to about 25 %, but the configuration of the sedimentation diagram showed no change. On boiling for two hours with dilute HCl (0.05 N) a diagram of another type was obtained. The amount dissolved was about 25 % of the wood, but all the substance sedimented with merely one boundary, forming a fairly symmetric peak in the diagram. It had a low sedimentation constant, 2.0—2.5, varying but slightly with concentration. The hydrolyzing effect of the acid had presumably depolymerized the hemicellulose rather completely, and also the cellulose to an appreciable degree, whence the peak obtained should correspond to the cellulose-component.

The effect of boiling with 0.1 N acetic acid, chlorine-substituted acetic acids or oxalic acid was quite the same as for hydrochloric acid.

The treatment of the wood with alkali had similar effects. All the experiments reported here were performed at room temperature and without exclusion of the air. 1 % NaOH did not change the general aspect of the original sedimentation diagram of the cuprammonium solution. On treatment with 10 % NaOH most of the hemicellulose-peak disappeared, but the sedimentation constant of the cellulose showed merely a slight decrease. The amount dissolved was 10—15 % of the wood. A treatment at a higher alkali concentration (18 %) gave about 25 % dissolution; only the cellulose-peak appeared, but with a low sedimentation constant (about 2).

From the experiments reported it might be concluded that chemical bonds exist between the lignin and the carbohydrates of wood. These bonds are hydrolyzed by warm dilute acid and by strong alkali. The hydrolysis of the lignin-carbohydrate bonds is more easily performed than that of the glucosidic bonds of the carbohydrate molecules, but the difference in the velocity of hydrolysis is quite small. However, it is possible, by the use of cold acid or of alkali of low concentration, to split a considerable amount of the lignin-carbohydrate bonds with merely slight depolymerization of the cellulose.

Various isolated wood celluloses, partly factory-made, partly prepared in the laboratory, were also examined in the ultracentrifuge. They were all completely soluble in cuprammonium.

By treating wood with sodium chlorite (Textone), it can be decomposed and the so-called *holocellulose* (Ritter and Kurth [64]) obtained in free state (Jayme [30, 31], Sohn and Reiff [75]). This cellulose, prepared in the laboratory, was examined here. The preparation was made as follows. The wood (spruce shavings)

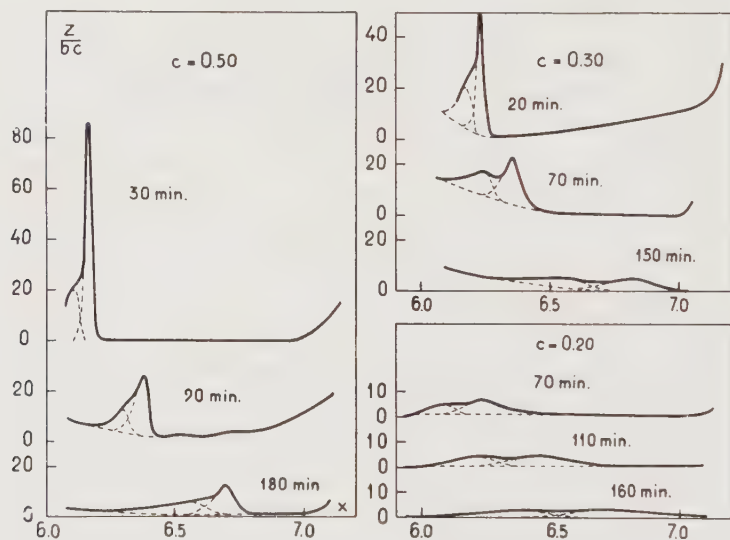


Fig. 11. Sedimentation diagrams of holocellulose from spruce wood.

was extracted with methanol-benzene and then treated with a sodium chlorite solution four times at 60° . The amount of wood was 3 % of the solution, and the sodium chlorite added was 30 % of the wood. In order to keep a suitable pH, 6 % of the wood weight of acetic acid was added. The first two treatments had a duration of 12 hours each and the two last ones of 8 hours each. Between the treatments the wood was washed with hot water. When the preparation was ready, the shavings still had a wooden structure. The yield was 74 % of the extracted wood.

In the sedimentation diagram two peaks were obtained (Fig. 11). 65 % of the total concentration was found to be in the

fastest sedimenting peak, and 35 % in the slowest one. At higher total concentrations this proportion seems to be changed in favour of the slowest component, but this must certainly be attributed to the effect mentioned on p. 16, according to which the left-hand side of a peak will be less steep than the right-hand side in higher concentrations (cf. the partition in Fig. 11).

The lignin was removed from the wood by the chlorite treatment, but the other constituents of wood, namely cellulose and hemicellulose, are still present. There is no doubt (compare the following preparation) that the slowest sedimenting substance is hemicellulose and the faster one cellulose. Sedimentation constants and $\frac{dB}{dx}$ were calculated for each component.

Table 9. *Holocellulose*.

Total conc.	Hemicellulose				Cellulose			
	<i>c</i>	<i>s</i>	<i>s · c</i>	$\frac{dB}{dx}$	<i>c</i>	<i>s</i>	<i>s · c</i>	$\frac{dB}{dx}$
0.5	0.175	2.0	0.35	0.48	0.325	3.2	1.04	0.18
0.3	0.105	2.4	0.25	0.52	0.195	4.2	0.82	0.33
0.2	0.070	2.6	0.18	0.64	0.130	4.8	0.62	0.54
0	0	3.2	—	0.83	0	7.2	—	1.20
		<i>k</i> = 3.4		γ_s = 0.45		<i>k</i> = 3.9		γ_s = 0.62

The sedimentation constant of cellulose is greater than that of hemicellulose, and its dependence on the concentration is also greater. It is of interest that the $\frac{dB}{dx}$ of cellulose is far more dependent on the concentration than that of hemicellulose. This fact is already apparent from Fig. 11. On extrapolation, $\left(\frac{dB}{dx}\right)_0$ is found to be higher for cellulose than for hemicellulose.

The holocellulose was treated with 18 % NaOH in a nitrogen atmosphere, in order to extract the hemicellulose and obtain pure α -cellulose.

The sedimentation diagrams show only one peak, which corresponds well with the cellulose peak of the holocellulose diagram. This confirms our interpretation of the latter diagram.

Table 10. *α -cellulose from holocellulose.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	2.5	1.25	0.16
0.30	3.3	0.99	0.25
0.20	4.0	0.80	0.51
0.10	4.9	0.49	0.80
0	6.5	—	1.29
	$k = 3.2$		$\gamma_s = 0.66$

The treatment with strong alkali has, however, affected the cellulose. The sedimentation constant and its dependence on the concentration is lower, and the polydispersity is higher. It is well known that alkaline treatment of cellulose causes oxidation by the oxygen of the air.

A technical *sulphate cellulose* from pine with 94.6 % α -cellulose and a technical cuprammonium-viscosity of 32 cp. (1 % concentration) showed the following sedimentation properties.

Table 11. *Sulphate cellulose.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.93	1.4	1.3	0
0.39	2.6	1.01	0.08
0.20	3.8	0.76	0.31
0.10	4.5	0.45	0.51
0	6.5	—	0.89
	$k = 3.9$		$\gamma_s = 0.48$

A *sulphite cellulose* ("ädelcellulosa" from spruce) with 97.1 % α -cellulose and 74 cp. technical cuprammonium-viscosity was also examined.

Table 12. *Sulphite cellulose.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
1.28	1.08	1.38	0
0.38	2.6	0.99	0.01
0.19	3.6	0.68	0.25
0.09	4.7	0.42	0.60
0	6.3	—	1.04
	$k = 3.8$		$\gamma_s = 0.54$

The sedimentation constant is a little lower and the polydispersity higher than for the sulphate cellulose. It is of interest to compare the marked difference in technical viscosity with the slight difference in sedimentation behaviour.

In some experiments with the sulphite cellulose, electrolytes were added to the solvent, in order to investigate electrostatic effects and their neutralization. The following results were obtained.

Table 13. *Sulphite cellulose in cuprammonium with the addition of electrolytes.*

Electrolyte added	c	s	$\frac{dB}{dx}$
0.25 M NaOH	(0.21)	5.80	—
0.25 M NaOH	(0.14)	3.98	0.60
0.2 M NaOH	0.19	4.21	0.30
0.1 M NaOH	0.23	3.98	0.26
0.2 M NaCl	(0.2)	2.51	—
0.2 M NaCl	(0.1)	2.92	—

On the addition of 0.25 M NaOH the cellulose did not dissolve completely, while on the addition of 0.2 M NaCl only about half of the cellulose dissolved. The concentrations given in brackets are the weighed amounts for solution. If higher amounts of NaOH than 0.3 M are added to the cuprammonium, the cellulose will not dissolve (cf. Hess and Messmer [21], p. 30). From Fig. 12 it will be seen that the addition of small amounts of NaOH has not noticeably affected the sedimentation constant. Thus it may be assumed that any electrostatic effects have already been neutralized by the electrolytes present in pure cuprammonium. An addition of sodium chloride appreciably diminishes the sedimentation constant. For further discussion cf. the diffusion measurements, p. 67—68.

In order to investigate the reproducibility of the molecular constants after certain chemical treatments, an *acetylation* and a *precipitation from cuprammonium* of the sulphite cellulose were carried out.

The method of acetylation was that described by Staudinger and Daumiller [85]. It was carried out in a mixture of acetic anhydride and pyridine. 3 g. cellulose was suspended in a mix-

ture of 155 ml. pyridine and 85 ml. acetic anhydride, and kept at 60° for 10 days. The cellulose acetate obtained was faintly brown in colour. It was thoroughly washed with water and dried in a desiccator over P_2O_5 . It was analysed by saponification in alcoholic sodium hydroxide in the cold, and found to contain 35.6 % acetyl, i.e. 1.6 acetyl groups per glucose unit. It was insoluble in acetone and chloroform. For the purpose of examina-

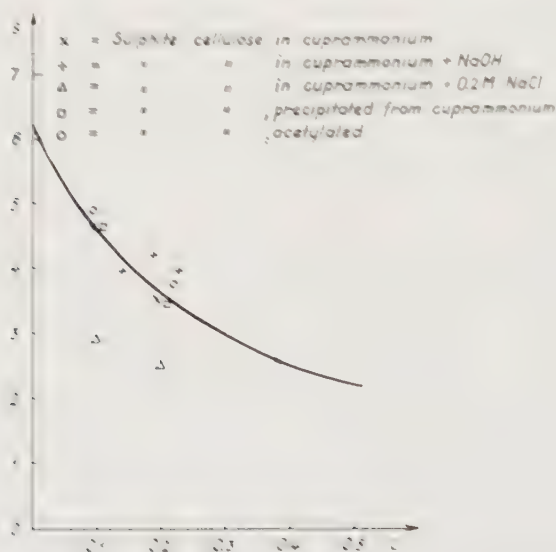


Fig. 12. The sedimentation constant as a function of the concentration for sulphite cellulose with different electrolytes added to the solution and with different pretreatments.

tion, it was dissolved in cuprammonium. The dissolution entails complete saponification.

The reprecipitation from cuprammonium was made with Seignette salt in a nitrogen atmosphere, according to the method described by Staudinger and Feuerstein [84]. The precipitated cellulose was washed with a Seignette salt solution in nitrogen and afterwards with water, whereupon it was dried in vacuo over P_2O_5 .

The sedimentation results for these two preparations are recorded in Table 14 and Fig. 12. They do not differ noticeably from the measurements of the non-treated cellulose.

Table 14. *Sulphite cellulose, acetylated, and precipitated from cuprammonium.*

	c	s	$\frac{dB}{dx}$
Acetylated	0.22	3.8	0.33
	0.09	4.9	0.53
Precipitated	0.21	3.5	0.37
	0.21	3.5	0.32
	0.11	4.7	0.56

In the viscose silk process, cellulose is treated with 18 % sodium hydroxide solution (mercerisation), the alkali removed by compressing, the remaining "alkali cellulose" shredded mechanically and left for "ageing" in the presence of air. The ageing process involves depolymerization. An *alkali cellulose* from a sulphite cellulose was aged for four days at 20°, regenerated by neutralization with sulphuric acid and carefully washed with water. The sedimentation examination in cuprammonium gave the following results:

Table 15. *Aged alkali cellulose.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	2.24	1.12	0.21
0.30	2.84	0.85	0.43
0.20	3.15	0.63	0.63
0.10	3.40	0.34	1.00
0	3.8	—	1.45
$k = 1.1$			$\gamma_s = 0.72$

The depolymerization appears in a decrease of the sedimentation constant and its dependence on the concentration. The polydispersity at the same time shows a rather marked increase.

Another alkali cellulose was left for ageing for about one month before regeneration. It had no fibrous structure.

This highly depolymerized cellulose has a very low sedimentation constant, which is almost independent of the concentration. Its polydispersity is very high. The measuring of $\frac{dB}{dx}$ is, of course, somewhat inaccurate where such high values are concerned.

Table 16. *Over-aged alkali cellulose.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	1.67	0.83	0.46
0.30	1.99	0.60	0.30
0.20	1.83	0.37	(1.36)
0.10	1.87	0.19	1.24
0	1.9	—	1.9
$k = 0.2$			$\gamma_s = 0.88$

From the alkali solution, which was pressed off after the mercerisation, so called β -cellulose was precipitated by neutralization with sulphuric acid. The β -cellulose was washed, dried and subjected to sedimentation investigation.

Table 17. β -cellulose.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	1.35	0.68	0.59
0.50	1.28	0.64	0.59
0.20	1.44	0.29	1.14
0.10	1.56	0.16	0.65
0	1.6	—	—
$k = 0.5$			

The sedimentation constant is somewhat lower than for the over-aged alkali cellulose, but the dependence on the concentration is more marked. The $\frac{dB}{dx}$ -calculation was extremely difficult and the results are not significant.

Two kinds of *viscose staple fibres* were examined¹. They were of "Phrix" manufacture, called BR from sulphite cellulose (spruce) and BR from sulphate cellulose (pine). The last-mentioned kind was made from sulphate cellulose of prehydrolyzed wood (Jayme [31], Correns[4]). Technical data regarding the fibres are given in the following table.

¹ The author is indebted to Professor E. Hägglund for supplying the staple fibres.

Table 18. *Technical data regarding BR from sulphite and sulphate celluloses.*

	BR from sulphite (spruce)	BR from sulphate (pine)
Titre, denier	1.58	1.45
Breaking length, km., dry	18.4	26.8
" " " " wet	12.3	17.3
Extensibility, %, dry	13.4	15.8
" " " " wet	16.3	22.4
Solubility in alkali, %	10.5	6.0
Pentosan, %	1.57	2.53

The centrifugal data are given in the following tables.

Table 19. *BR from sulphite cellulose (spruce).*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	2.15	1.08	0.44
0.30	2.30	0.69	0.62
0.20	2.46	0.49	0.77
0.10	2.47	0.25	1.06
0	2.6	—	1.43
	$k = 0.5$		$\gamma_s = 0.71$

Table 20. *BR from sulphate cellulose (pine).*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	2.15	1.08	0
0.30	2.72	0.72	0.30
0.20	3.25	0.65	0.44
0.20	3.12	0.62	0.49
0.10	3.56	0.36	0.80
0	4.1	—	1.07
	$k = 1.7$		$\gamma_s = 0.56$

The higher tensile strength of the rayon from sulphate cellulose corresponds to a higher sedimentation constant and a lower polydispersity.

b. The Sedimentation of Cellulose Nitrate in Acetone.

Cellulose nitrate was prepared from different cellulose raw materials, being partly the same as were used for the studies of

cellulose in cuprammonium. All the nitrates examined were prepared in the laboratory. The purpose was a comparison of the molecular size and shape of the cellulose molecules before and after nitration. In order as far as possible to avoid depolymerization (Staudinger and Mohr [86]), the nitration was not made with sulphuric acid as a water absorbent, but with phosphoric acid. The nitration mixture used had the composition 40 % HNO_3 , 40 % H_3PO_4 (calculated as free from water of crystallization), and 20 % P_2O_5 . The nitration was made in the following way:

0.5 g. cellulose was carefully divided in a defibrator or by means of cards and dried in vacuo over P_2O_5 or silica gel. To the dry cellulose 25 ml. of the nitration acid, cooled to -10° , was added. The acid and cellulose were well mixed with a glass rod, the reaction vessel was closed with a ground glass stopper and placed in an ice bath (0°). After 6 hours the acid was rapidly removed by sucking through a sintered glass filter (Jena G 3), and the nitrated cellulose immediately washed with cold (-10°) 50 % acetic acid several times, and then thoroughly washed with water. It was kept in a large volume of water till the next day, and then stabilized by boiling four times for half an hour in water. It was stored moistened with water, and before use was dried in vacuo over P_2O_5 . Analyses of a few of the cellulose nitrates showed that they contained about 13.8 % N.

The shape of the sedimentation curves of cellulose nitrate in acetone is quite similar to that of cellulose in cuprammonium. It was found, however, that the relation (6) with a constant k is in general valid for the cellulose nitrates at lower concentrations only. At higher concentrations, k will have a lower value.

For the $\frac{dB}{dx}$ -calculations the value $\frac{dn}{dc} = 118 \cdot 10^{-5}$ was used (cf. Mosimann [55], p. 388). The results are recorded in the following tables. The values of k given are those obtained at low concentrations.

The holocellulose, prepared by chlorite treatment of spruce wood, was also nitrated. The sedimentation diagrams showed the same results as when examined in cuprammonium: the hemi-cellulose sedimented behind the cellulose. The proportion was

Table 21. *Cellulose nitrate of unbleached American linters.*

c g./100 ml.	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.15	3.08	0
0.20	10.6	2.12	0
0.15	11.2	1.68	0.04
0.10	13.8	1.38	0.06
0.05	15.4	0.77	0.12
0	19.0	—	0.21
$k = 4.2$			$\gamma_s = 0.12$

Table 22. *Cellulose nitrate of bleached American linters.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.2	3.10	0
0.20	9.1	1.82	0.03
0.15	10.1	1.52	0.05
0.10	10.5	1.05	0.06
0.05	12.3	0.62	0.16
0	14.0	—	0.27
$k = 2.8$			$\gamma_s = 0.15$

Table 23. *Cellulose nitrate of chlorite bleached linters.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	5.7	2.85	0
0.20	9.6	1.92	0
0.15	10.1	1.52	0
0.10	11.8	1.18	0.05
0.05	15.1	0.76	0.20
0	18.5	—	0.40
$k = 5.0$			$\gamma_s = 0.22$

Table 24. *Nitrate of sulphate cellulose (same as in Table 11).*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.2	3.10	0
0.20	9.5	1.90	0
0.15	10.4	1.56	0.09
0.10	12.1	1.21	0.17
0.05	13.9	0.70	0.29
0	16.2	—	0.46
$k = 3.5$			$\gamma_s = 0.26$

Table 25. Nitrate of sulphite cellulose (same as in Table 12).

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.2	3.1	0
0.20	8.8	1.76	0
0.15	10.6	1.59	0.02
0.10	12.1	1.21	0.21
0.05	13.8	0.69	0.32
0	16.4	—	0.61
$k = 3.6$			$\gamma_s = 0.33$

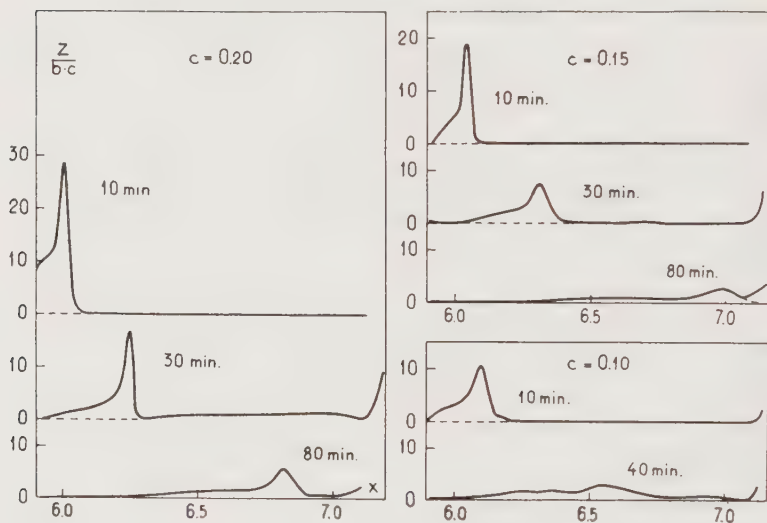


Fig. 13. Sedimentation diagrams of cellulose nitrate of holocellulose.

about the same, 35 % hemicellulose and 65 % cellulose. This shows that the hemicellulose is likewise disposed for nitration. It is known (Hägglund [13], p. 119) that spruce wood hemicellulose largely gives mannose on hydrolysis. It is possible that the mannan gives a soluble nitrate (cf. Husemann [26, 27]). In the sedimentation diagrams (Fig. 13) the hemicellulose part of the curve was very widespread and it was not possible to calculate any sedimentation constant or $\frac{dB}{dx}$ for it. For the cellulose part the results are given in Table 26.

Table 26. *Nitrate of holocellulose (same as cellulose part of Table 9).*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.325	7.1	2.31	0
0.130	11.7	1.52	0.11
0.098	13.2	1.29	0.24
0.065	15.4	1.00	0.46
0	21.6	—	1.02
	$k = 4.2$		$\gamma_s = 0.54$

After treatment with 18 % NaOH (made without exclusion of the air), only the cellulose remained, and the sedimentation diagram of the corresponding nitrate was quite similar to that of the α -cellulose in cuprammonium.

Table 27. *Nitrate of α -cellulose from holocellulose.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.7	3.35	0.01
0.20	9.8	1.96	0.04
0.15	10.1	1.52	0.19
0.10	11.0	1.10	0.49
0.05	12.1	0.60	0.90
0	13.4	—	1.33
	$k = 2.1$		$\gamma_s = 0.67$

The comparison between the molecular constants and the polydispersity calculations of cellulose in cuprammonium and the corresponding nitrates will be discussed in Chapter IV.

Several sulphite celluloses (pulps for rayon manufacture) were also examined after nitration. Technical data regarding the rayon pulps and the results of the sedimentation investigations are given in the following tables.

Table 28. *Technical data regarding rayon pulps.*

Pulp No.	α -content, %	Cuprammonium viscosity (1 % solution), cp.
1	92.0	25.6
2	94.1	36.4
3	89.9	23.9
4	91.0	13.5
5	89.4	26.3
6	98.3	57

Table 29. *Cellulose nitrate of Rayon pulp No. 1.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.5	3.25	0
0.30	8.2	2.46	0
0.20	10.1	2.02	0.05
0.15	10.8	1.62	0.26
0.10	10.9	1.09	0.30
0.05	14.1	0.71	0.48
0	16.7	—	0.77
$k = 3.6$			$\gamma_s = 0.42$

Table 30. *Cellulose nitrate of Rayon pulp No. 2.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.5	3.25	0.01
0.20	9.4	1.88	0.03
0.15	10.8	1.62	0.17
0.10	11.9	1.19	0.25
0.05	14.8	0.74	0.52
0	18.3	—	0.73
$k = 4.8$			$\gamma_s = 0.40$

Table 31. *Cellulose nitrate of Rayon pulp No. 3.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.7	3.4	0.02
0.20	10.2	2.04	0.06
0.15	10.9	1.63	0.15
0.10	13.2	1.32	0.42
0.05	13.4	0.67	0.71
0	15.5	—	1.06
$k = 2.6$			$\gamma_s = 0.55$

Table 32. *Cellulose nitrate of Rayon pulp No. 4.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.8	3.4	0.02
0.20	9.6	1.92	0.15
0.15	10.2	1.53	0.29
0.10	11.9	1.19	0.42
0.05	14.2	0.71	—
0	17.6	—	1.00
$k = 4.8$			$\gamma_s = 0.53$

Table 33. *Cellulose nitrate of Rayon pulp No. 5.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.6	3.3	0
0.20	10.0	2.0	0.03
0.15	11.2	1.68	0.27
0.10	12.4	1.24	0.44
0.05	14.3	0.72	0.68
0	16.8	—	1.00
$k = 3.4$			$\gamma_s = 0.53$

Table 34. *Cellulose nitrate of Rayon pulp No. 6.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	6.2	3.1	0
0.20	8.8	1.76	0
0.15	10.4	1.56	0.05
0.10	10.9	1.09	0.09
0.05	14.6	0.73	0.29
0.03	17.3	0.52	0.41
0	23.3	—	0.60
$k = 11.5$			$\gamma_s = 0.33$

c. The Sedimentation of Sodium Cellulose Xanthate.

Sodium cellulose xanthate is soluble in alkaline aqueous solutions, where it will be electrolytically dissociated. The high-molecular compound is thus highly charged. The sedimentation of this heavy molecule is retarded, owing to the electrostatic

Table 35.

Electrolyte concentration	s
0	1.40
0.20 M NaOH	1.77
0.51 M NaOH	2.16
1.00 M NaOH	2.36
1.09 M NaOH	2.30
1.50 M NaOH	2.58
2.05 M NaOH	2.54
2.05 M NaOH	2.56
0.20 M NaOH + 1.0 M NaCl	2.24
0.20 M NaOH + 1.0 M NaCl	2.24

attraction from the lighter sodium ions. This effect is diminished, and can be eliminated, by the addition of non-sedimenting electrolytes. In the experiments of Table 35 a viscose solution containing 7 % cellulose and 1.5 M NaOH was diluted to 0.2 % cellulose

with different electrolyte solutions.

The dependence on the electrolyte concentration is illustrated in Fig. 14. It will be seen that the charge effects are not eliminated until we reach an electrolyte concentration of 1.0—1.5 M. This shows that the dissociation of sodium cellulose xanthate is very marked.

Sedimentation experiments have been made with several xanthates. The mode of xanthate preparation was that described by Lottermoser and Wulsch [47].

In some experiments ordinary viscose solutions were simply diluted, in others an isolated sodium cellulose xanthate was dissolved in a suitable salt solution. This

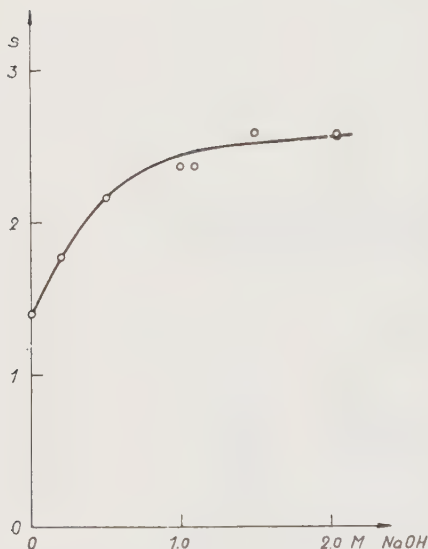


Fig. 14. The dependence of the sedimentation constant of sodium cellulose xanthate on the concentration of NaOH.

xanthate had been purified by washing it with ice-cooled absolute alcohol immediately after the termination of the xanthation, thus removing superfluous alkali and carbon disulphide. This washing does not hydrolyze the xanthate (Staudinger and Zapf [88]). The xanthate is stored in vacuo over a drying agent, as moisture and carbon dioxide very soon demolish it. On analysis it proved to contain about 18.5 % S and 12.7 % Na, corresponding to about 0.77 dithiocarbonate groups per glucose unit, and an extra alkali of about 0.7 mole per glucose unit, which could not be washed away.

The ageing time and temperature of the alkali cellulose were varied in the different preparations. The viscosity of the viscoses obtained therefore shows great variation (see Table 36).

Table 36. *Ageing of alkali cellulose for viscose preparations.*

No.	Ageing time (hours)	Ageing temp.	Viscosity of 6 % cellulose solution, poise
1	96	18°.5	32
2 { 66 %	96	18°.5	over 100
{ 34 %	3	18°.5	
3 (commercial manufacture)	93	18°.5	18
8	95	17°.5	28
9 { 90 %	95	17°.5	37
{ 10 %	3	17°.5	
10	100	20°	14
11 { 90 %	140	20°	20
{ 10 %	25	20°	
12	100	20°	34
15 ¹	100	20°	27

The following tables give the results of sedimentation analysis of the xanthates and viscoses. The concentrations are calculated as pure cellulose. From diffusion experiments dn/dc was found to be $231 \cdot 10^{-5}$ (cf. p. 88), and this value was used for the determination of the area in $\frac{dB}{dx}$ -calculations. The sedimentation constants in the Tables 35 and 37—47 are reduced to pure water.

Table 37. *Viscose No. 1, solvent 1.31 M NaOH + 0.12 M CS₂.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.77	1.38	1.06	0.16
0.41	1.71	0.70	0.35
0.20	1.96	0.39	0.57
0	2.30	—	0.85
	$k = 0.9$		$\gamma_s = 0.45$

Table 38. *Viscose No. 2, solvent 1.31 M NaOH + 0.12 M CS₂.*

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.40	2.07	0.83	0.16
0.20	2.69	0.54	0.35
0.10	3.43	0.34	0.62
0	4.4	—	1.03
	$k = 2.8$		$\gamma_s = 0.54$

¹ This alkali cellulose was washed with 18 % NaOH immediately before the sulphiding.

Table 39. *Viscose No. 3*, solvent 1.31 M NaOH + 0.12 M CS₂.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.40	2.05	0.82	0.18
0.20	2.57	0.51	0.29
0.10	2.76	0.28	0.41
0	3.1	—	0.58
	$k = 1.3$		$\gamma_s = 0.32$

Table 40. *Sodium cellulose xanthate No. 8*, solvent 0.2 M NaOH + 1.0 M NaCl.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.67	1.73	1.16	0.33
0.27	2.20	0.60	0.61
0.134	2.18	0.292	0.69
0.067	2.35	0.157	0.84
0	2.40	—	0.93
	$k = 0.7$		$\gamma_s = 0.49$

Table 41. *Sodium cellulose xanthate No. 9*, solvent 0.2 M NaOH + 1.0 M NaCl.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.67	1.75	1.17	0.30
0.27	2.16	0.58	0.52
0.134	2.36	0.315	0.63
0.067	2.60	0.175	0.68
0	2.70	—	0.74
	$k = 0.8$		$\gamma_s = 0.40$

Table 42. *Sodium cellulose xanthate No. 10*, solvent 0.2 M NaOH + 1.0 M NaCl.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.67	1.75	1.17	0.25
0.345	2.10	0.71	0.46
0.134	2.32	0.31	0.69
0.067	2.40	0.16	0.86
0	2.50	—	1.04
	$k = 0.6$		$\gamma_s = 0.54$

Table 43. *Sodium cellulose xanthate No. 11*, solvent
0.2 M NaOH + 1.0 M NaCl.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.67	1.71	1.15	0.37
0.345	2.08	0.72	0.52
0.134	2.12	0.28	0.63
0	2.40	—	0.78
	$k = 0.6$		$\gamma_s = 0.42$

Table 44. *Viscose No. 12*, solvent 0.2 M NaOH + 1.0 M NaCl.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.20	2.24	0.45	0.61
0.10	2.60	0.26	0.86
0	2.80	—	1.10
	$k = 1.0$		$\gamma_s = 0.57$

Table 45. *Viscose No. 15*, solvent 0.2 M NaOH + 1.0 M NaCl.

c	s	$s \cdot c$	$\frac{dB}{dx}$
0.50	1.92	0.96	0.44
0.20	2.29	0.46	0.53
0.10	2.61	0.26	0.72
0	2.80	—	0.90
	$k = 0.9$		$\gamma_s = 0.48$

Some centrifugations were made in order to study the effect of the viscose ripening. The degree of ripeness was measured in terms of the NaCl-concentration necessary for coagulation. The cellulose concentration in the sedimentation runs was always 0.3 %.

The ripening seems to have no effect on the sedimentation constant. It is of interest to note that even when the electrolytes added are not sufficient for neutralization of the charge effect, the ripening does not change the sedimentation velocity (exps. No. 1—5, 2—6, 3—7, Table 46).

Table 46. *Viscose ripening.*

Exp. No.	NaCl point (degree of ripeness)	Solution for dilution		<i>s</i>
		M NaOH	M NaCl	
1	8 %	0.26	—	1.52
2	7 %	0.26	0.2	1.71
3	7 %	0.26	0.86	1.93
4	5 %	0.26	1.00	1.88
5	3 %	0.26	—	1.49
6	3 %	0.26	0.2	1.68
7	3 %	0.26	0.86	1.91

d. The Sedimentation of Sodium Cellulose Glycollate.

Only one preparation was investigated. The product is certainly rather depolymerized. It was dissolved in a neutral salt solution. The sedimentation curves show one, fairly symmetrical peak. The results are summarized in the following table.

Table 47. *Sodium cellulose glycollate.*

M NaCl	<i>c</i>	<i>s</i>	<i>s · c</i>	$\frac{d B}{d x}$
0.2	0.20	1.78	—	—
1.0	0.50	2.01	1.00	0.18
1.0	0.30	2.33	0.70	(0.35)
1.0	0.20	2.51	0.50	(0.24)
1.0	0.10	3.02	0.30	0.46
	0	3.4	—	0.60
		<i>k</i> = 1.3		$\gamma_s = 0.33$

Diffusion.

1. Earlier Measurements on Cellulose.

Herzog and Krüger [18], using Öholm's method [58], reported that cellulose in cuprammonium has a diffusion constant of about $2.4 \cdot 10^{-7}$ cm²/sec, and that it obeys Fick's diffusion law. Cellulose nitrate has been subjected to diffusion measurements by Krüger and collaborators [19, 39]. They found that the cellulose nitrate does not obey Fick's law and that the deviations could not be explained simply by the dependence of the diffusion constant on the concentration. They assumed an affinity of the cellulose nitrate molecules to each other and to the molecules of the solvent. The results which they obtained may possibly have been due to the polydispersity. Cellulose derivatives were investigated by Polson [61], who used Lamm's scale method [41] for observation and found that the diffusion curves obtained are skew. He showed that this could be accounted for by the swelling pressure, described by Ostwald [59]. Diffusion measurements on cellulose nitrates have been reported also by Gralén [11].

2. Method and Diffusion Cells.

The use of Lamm's scale method, founded on refractive index differences, has afforded the best facilities for diffusion measurements. The arrangement is the same as for sedimentation measurements in the ultracentrifuge.

For measurements in aqueous solutions (xanthate, glycollate) the slide cell of Lamm ([42], p. 20, [45]) has been employed. It was not possible, however, to adapt it for use in nitrogen atmosphere, as it could not be made air-tight for evacuation. It was thus unsuitable for use with the cuprammonium solutions. An

attempt to adapt the cell construction of Neurath [57] for that purpose was not successful. A glass cell was then used instead, (see Fig. 15). This is a slight modification of Svedberg's construction ([90], p. 141), also used by Tiselius and Gross [94] and others. The devices for filling are illustrated in Fig. 16. The

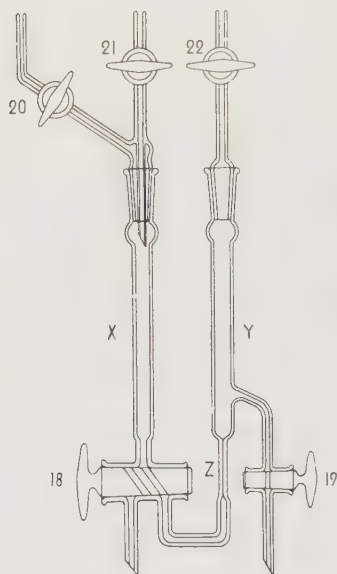


Fig. 15. Diffusion cell of glass for work in a nitrogen atmosphere.

tube and cock 20 is intended for evacuation and filling with nitrogen. Through the tube and cock 19 the solution is filled into the tube Y, the capillary Z and the three-way cock 18. The solvent is then filled through the cock 21 into the diffusion tube X, which is a selected tube of optically uniform glass. The boundary is formed by turning the cock 18 and is shifted slowly up to the middle of the tube X by a low over-pressure of nitrogen in the tube Y. The whole experiment is carried out in a thermostat, as a rule at 20°.

For the cellulose nitrate solutions in acetone a glass cell was also used, but without the additional tubes 19 and 20. The cocks were lubricated with ordinary tap fat, used very charily and not in immediate proximity to the

tap holes. This mode of lubrication has worked very well and has not caused any disturbances (cf. Polson [61], p. 174).

The diffusion of threadlike molecules is a very slow process. This was found especially in regard to cellulose in cuprammonium. An experiment of that type often has a duration of 8—10 days. In order to gain time, two diffusion cells of the glass type were used in the same thermostat. By a slight lateral displacement (about 20 mm.), the cells could alternatively be moved into the light path for observation and photographing. A similar arrangement was made also for two slide cells, shifting about 60 mm. The cells hang on a stand, sliding on horizontal, plane, lubricated, metallic surfaces, and the movement is transmitted by a toothed wheel. No drawback (owing to vibration or so) has re-

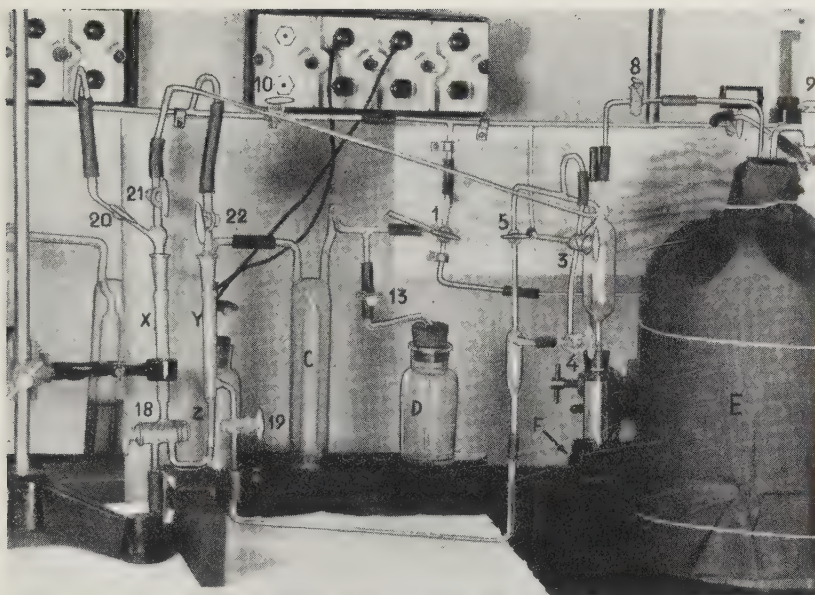


Fig. 16. Photograph of the arrangement for filling the diffusion cell of Fig. 15. For explanation cf. Fig. 4.

sulted from this arrangement. For the glass cells, the two experiments could be started at the same time, the cells being connected with a T-tube to the pressure flask.

3. The Diffusion Curve and the Polydispersity Determination.

The diffusion constant, calculated from the diffusion in one direction with infinite vessel limits, is determined by Wiener's equation [99]

$$\frac{dn}{dx} = \frac{n_1 - n_0}{2\sqrt{\pi D t}} \cdot e^{-\frac{x^2}{4Dt}} \quad (23)$$

Here D is the diffusion constant, t is the time after start, x is the distance from the original boundary, and $n_1 - n_0$ is the refractive index difference between solution and solvent. This equation is valid for a substance uniform in D , provided that D and $\frac{dn}{dc}$ are constants for the concentration interval adopted.

The scale method of Lamm gives $\frac{dn}{dx}$ as a function of x . In the following, $\frac{dn}{dx}$ will be simply noted y . In the ideal case the curve is a normal distribution curve with the maximum at the original boundary position. Lamm [42], p. 33 ff., has given several equations for the calculation of the diffusion constant from this curve.

If the diffusing substance contains several molecular species of different sizes, each one diffusing ideally, the resulting curve will be the sum of several diffusion curves with a common axis. The theory of this case has been treated by the author [11], and a short extract will be given here.

Wiener used the formula

$$D_A = \frac{A^2}{4\pi t H^2} \quad (24)$$

for the calculation of the diffusion constant. A denotes the area between the curve and the x -axis, and H is the maximum height of the curve. The notation D_A means the "area" method of calculation.

To the formula (24) and other formulas for the calculation of diffusion constants, a factor including experimental constants should be applied (Lamm [44], p. 696). This factor is

$$\left(\frac{l-b}{l \cdot G} \right)^2$$

where G is the photographic enlargement, l the distance from the scale to the objective, and b the distance between the scale and the middle of the cell. It has been deliberately omitted in this theoretical discussion.

It will be assumed that the refractive index increment $\frac{dn}{dc}$ is a constant, not only for the concentration interval adopted, but also for the different components in the mixture. This assumption is in general legitimate for a polydisperse system, where the chemical constitution of the components is very much the same. For a single component with the diffusion constant D_i and giving the curve area dA and the height dH , we get

$$dA = 2 V \overline{\pi D_i t} \cdot dH.$$

Integration and comparison with (24) gives

$$A = \int dA = 2 V \overline{\pi t} \int V \overline{D_i} dH = 2 V \overline{\pi t} V \overline{D_A} \cdot H \quad (25)$$

or

$$V \overline{D_A} = \frac{\int V \overline{D_i} dH}{H} = \frac{\int dA}{\int \frac{dA}{V \overline{D_i}}}$$

As dA is proportional to the concentration dc , we get

$$V \overline{D_A} = \frac{\int dc}{\int \frac{dc}{V \overline{D_i}}} = \frac{c}{\int \frac{dc}{V \overline{D_i}}}$$

or

$$D_A = \left(\frac{c}{\int \frac{dc}{V \overline{D_i}}} \right)^2. \quad (26)$$

The above equation defines an average of the D_i s, which is obtained by using equation (24) for the whole curve. If the component number is limited, it may be written

$$D_A = \left(\frac{\sum_i c_i}{\sum_i \frac{c_i}{V \overline{D_i}}} \right)^2 \quad (27)$$

This formula was derived and used by Quensel[62], p. 84.

Another formula, often used for diffusion constant calculation, is

$$D_m = \frac{m^2}{2 t A} \quad (28)$$

where m_2 is the second moment of the curve about the vertical axis through the arithmetic medium of the curve. It is given by the equation

$$m_2 = \int_{-\infty}^{+\infty} x^2 y dx. \quad (29)$$

In general the position of the point $x=0$ is not known, and the moments $m'_1 = \int (x-b) \cdot y \cdot dx$ and $m'_2 = \int (x-b)^2 \cdot y \cdot dx$ are calculated about an arbitrary, vertical axis at the distance b from $x=0$, and m_2 is determined by the equation

$$m_2 = m'_2 - \frac{(m'_1)^2}{A}.$$

For the determination of b we have

$$b = -\frac{m'_1}{A}$$

(Yule and Kendall [101], p. 154 f.).

The notation D_m means calculated by the "moment" method. Lamm has used this method of calculation for "normal analysis" of the curves. By similar reasoning as for D_A we obtain for a mixture

$$d m_2 = 2 D_i t dA$$

and

$$m_2 = \int d m_2 = 2 t \int D_i dA = 2 t D_m A \quad (30)$$

because the sum of the components' moments is equal to the moment of the total curve. Thus

$$D_m = \frac{\int D_i dA}{A} = \frac{\int D_i dc}{c} \quad (31)$$

or, written as a sum

$$D_m = \frac{\sum_i c_i D_i}{\sum_i c_i} \quad (32)$$

i. e. a weight average of the diffusion constants.

Other formulas for the calculation of the diffusion constant give other averages. For details the reader is referred to the original work (Gralén [11]).

The ratio D_m/D_A is theoretically always greater than unity, which means that the experimental curve of a polydisperse sub-

stance always shows a greater height, H , than the corresponding normal curve, or shows a "positive excess" (Lamm [42], p. 39). The ratio D_m/D_A gives a measure of the polydispersity. It must be emphasized that a high experimental accuracy is necessary for this calculation. The position of the base line of the curve is of particular importance. This line has therefore always been determined by adopting a constant curve area for all exposures throughout the experiment, a similar arrangement as when calculating $\frac{dB}{dx}$ from sedimentation curves (p. 18).

In analogy with Lansing and Kraemer's assumption for the molecular weights, equation (18), a logarithmic distribution function could be arbitrarily assumed for the diffusion constants

$$dc = K_D \cdot e^{-y^2} dy \quad (33)$$

where

$$y = \frac{1}{\gamma_D} \log (D/D_1).$$

Here K_D is a constant, the maximum height of the distribution curve, γ_D is the distribution coefficient for the diffusion constants, and D_1 is the diffusion constant at the maximum point of the distribution curve. As for γ_s (p. 20), a certain relation to the non-uniformity coefficient β can be found. This matter is discussed in Chapter IV.

It can be shown by simple mathematical reasoning that on assumption of the distribution (33) the relation

$$D_A/D_1 = D_m/D_A = e^{3\gamma_D^2/8} \quad (34)$$

is valid.

4. The Skew Diffusion Curve.

On the diffusion of starch, Lamm ([42], p. 99 ff.) found that the diffusion curves assume an asymmetrical shape, the part facing the solvent being steeper than that facing the solution. Fig. 17 shows a curve of that shape. In the case of starch, this effect disappeared on the addition of low-molecular electrolytes, which indicates that the skewness is due to charges of the col-

loidal amylopectin. Polson [61] found skew diffusion curves for some high-molecular fractions of methylcellulose and cellulose acetate, and ascribed the effect to the swelling pressure, which causes a dependence of the diffusion constant on the concentration, according to the equation

$$D_c = D_0 \left(1 + \frac{K a}{R T} \cdot c^{K-1} \right) \quad (35)$$

where a and K are constants and D_0 is the diffusion constant at $c = 0$. This equation was derived from Ostwald's [59] equation

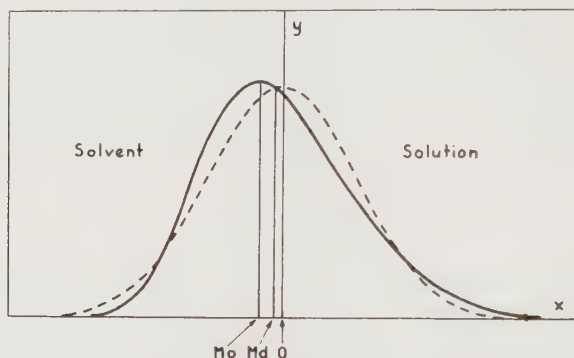


Fig. 17. Skew diffusion curve.

$x = 0$ is the position of the original boundary (the arithmetic mean), Md = the median, Mo = the maximum point (the mode).

for the swelling pressure p_s , which is additional to the osmotic pressure:

$$p = p_0 + p_s \quad (36)$$

and

$$p_s = a \cdot c^K.$$

From osmotic measurements by Schulz, Polson calculated K to be constant for cellulose nitrates of different molecular weights, whereas a varied. As K has a value around 2, the dependence of D on the concentration would be almost linear.

If D is dependent on the concentration, the diffusion constant can be calculated from the diffusion curve by means of Boltzmann's equation [2]

$$D = \frac{1}{2ty} \int_x^x x y dx. \quad (37)$$

This equation is valid independently of the form of the concentration function. We propose the problem of calculating a weight average of the diffusion constants of this curve, assuming no polydispersity. The equation (37) is valid for a concentration interval dc proportional to $y dx$, and by integration we get

$$\frac{\int D dc}{\int dc} = \frac{\int_{-\infty}^{+\infty} \frac{y dx}{2 t y} \int_x^{\infty} x y dx}{\int_{-\infty}^{+\infty} y dx} = \frac{1}{2 t} \cdot \frac{\int_{-\infty}^{+\infty} x^2 y dx}{\int y dx} = \frac{m_2}{2 t A} \quad (38)^1$$

i. e. we obtain the moment formula valid for the weight average, also if D is dependent on the concentration. It was shown above (p. 58) that it is valid for a polydisperse substance, and thus it could be very generally applied.

For the area formula, no such general application can be shown. When applied to a skew curve, it has not the same definite significance as the moment formula. In the case of moderate skewness, however, it is of some value for the characterization of the substance.

For a skew curve, different mid points must be distinguished (see Fig. 17). Of special importance are the arithmetic mean, the median and the maximum point. The arithmetic mean, $x = 0$, is determined so that

$$\int_{-\infty}^{+\infty} x y dx = 0. \quad (39)$$

This point corresponds to the original boundary position of the diffusion experiment. The perpendicular through the median, Md , divides the area of the curve into two equal parts. The maximum point, Mo (mode), is still far removed from the original boundary.

¹ For this deduction the equation (39) is necessarily postulated. By partial integration is found

$$\int_{-\infty}^{+\infty} dx \int_x^{\infty} x y dx = \int_{-\infty}^{+\infty} x^2 y dx + \left[x \int_x^{\infty} x y dx \right]_{-\infty}^{+\infty}$$

and the last term is certainly 0, because y approaches 0 about as e^{-x^2} when $x \rightarrow \infty$.

For moderately skew curves, we have approximately

$$M_0 = 3 M d. \quad (40)$$

(Yule and Kendall [101], p. 125).

When diffusion is proceeding, the arithmetic mean should remain at the same position in the diffusion cell, whereas Md and M_0 shift their position, starting from the position of the arithmetic mean.

If the dependence of D on concentration is linear, it may be written

$$D = D_0(1 + k_1 c) \quad (41)$$

where k_1 is a constant.

We have

$$c = \int_{-\infty}^x \frac{dc}{dx} dx = \frac{1}{dn/dc} \int_{-\infty}^x y dx. \quad (42)$$

By applying Boltzmann's equation, we obtain

$$-\frac{1}{2ty} \int_{-\infty}^x xy dx = D_0 \left(1 + \frac{k_1}{dn/dc} \int_{-\infty}^x y dx \right),$$

and derivation with regard to x gives

$$\frac{1}{2ty^2} \cdot \frac{dy}{dx} \cdot \int_{-\infty}^x xy dx - \frac{x}{2t} = \frac{k_1 D_0 y}{dn/dc}. \quad (43)$$

This equation affords a possibility of determining k_1 from any point of the curve. Particularly simple is the expression for the maximum point, where $\frac{dy}{dx} = 0$, $x = M_0$, and $y = H$. This gives

$$k_1 = - \frac{M_0 \frac{dn}{dc}}{2t D_0 H} \quad (44)$$

or

$$k_1 = - \frac{M_0}{2t D_0 \cdot \left(\frac{dc}{dx} \right)_{\max.}} \quad (45)$$

In general, M_0 is negative and thus k_1 positive.

If equation (41) is valid, we have obviously

$$D_m = D_0 \left(1 + \frac{k_1 c_1}{2} \right) \quad (46)$$

where c_1 is the concentration in the lower part of the cell at the beginning of the experiment. Substitution gives

$$D_0 = D_m + \frac{M_0 c_1}{4 t \cdot \left(\frac{dc}{dx} \right)_{\max.}} = D_m + \frac{A \cdot M_0}{4 H t} \quad (47)$$

5. Results of Diffusion Measurements.

a. The Diffusion of Cellulose in Cuprammonium.

The diffusion of cellulose in cuprammonium shows several deviations from the ideal diffusion.

The calculations of D_m were made by plotting the values of $\frac{m_2}{A}$ (also called the square of standard deviation, σ^2) against t in a chart. This procedure should theoretically give a straight line through the origin $t=0$, $\sigma^2=0$. From the angle between this line and the t -axis the diffusion constant can be calculated. A similar method has been adopted for the calculation of D_A , plotting the values of the quotient $(A/H)^2$ against t in a diagram. The experiments accord very well with a straight line. However, it frequently does not pass through the origin, but crosses the t -axis at a certain positive time, may be one or two days. This would signify that the diffusion starts some time after the boundary was formed, or that the diffusion at first proceeds at a slower rate, afterwards asymptotically finding its definitive rate. In view of the steepness of the diffusion curves at the beginning of an experiment, which causes difficulties in calculation, it is not easy to decide between these two possibilities. The last-mentioned would seem to be the most probable, as is indicated by some experiments (see p. 65).

In general, the diffusion constant is dependent on the concentration, which causes a skewness of the diffusion curve. The elaborate calculation with Boltzmann's equation has been made

in some cases, and it has been found that the dependence on concentration is almost linear. In most cases therefore, the equation (41) has been assumed, and the calculation has been made according to the simple equation (47) after determining D_m by the moment method. This gives D_0 , the diffusion constant at infinite dilution, which could be used for molecular weight calculations. Several exposures from every experiment have been measured and averages taken of the correction term $\frac{A M_0}{4 H t}$. For this calculation, the zero-point $t=0$ was taken at the point of intersection in the (t, σ^2) -chart between the time-axis and the straight line joining the points from the different exposures (cf. p. 63 and Fig. 18).

As a rule, the quotient D_m/D_A was also calculated, even if the significance of D_A is somewhat doubtful when the curves are skew. It was frequently found that D_m/D_A , contrary to the theory, had a value less than unity. Obviously it could not be used for polydispersity determination.

The results of the measurements are given in the following table, after which a few of the experiments are recorded and

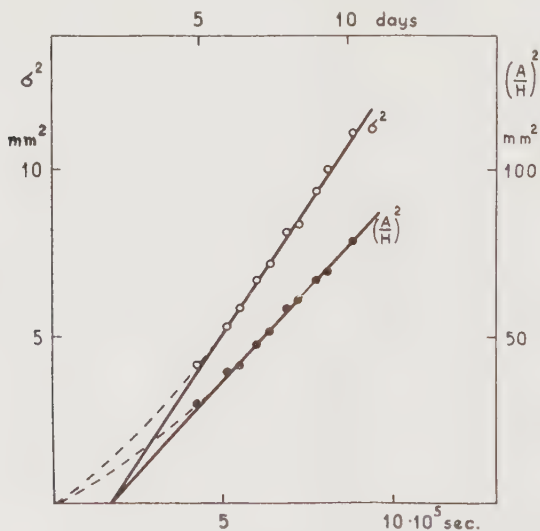


Fig. 18. The calculation of diffusion constants for an experiment with sulphite cellulose.

Abscissa: the time after start. Ordinate: the square of the standard deviation (σ^2), and the quotient $(A/H)^2$.

Table 48. *Diffusion of cellulose in cuprammonium.*

Cellulose	Conc.	D_m	D_A	D_m/D_A	$-\frac{A M_0}{4 H t}$	k_1	D_0
Raw Georgia Cotton	0.20	0.34	0.34	1.00	0.14	7.0	0.20
Unbleached American linters . .	0.38	0.50	0.48	1.04	0.25	5.3	0.25
" " " "	0.165	0.34	0.34	1.00	0.12	6.6	0.22
" " " " " "	0.065	0.28	0.28	1.00	0.05	6.4	0.23
Bleached American linters . . .	0.52	0.80	0.84	0.95	0.22	1.5	0.58
" " " " " "	0.20	0.66	0.67	0.99	0.11	2.0	0.55
" " " " " "	0.10	0.46	0.47	1.00	0.06	3.0	0.40
" " " " " "	0.09	0.48	0.50	0.96	0.05	2.6	0.43
Chlorite bleached linters	0.20	0.39	0.39	1.00	0.13	5.0	0.26
Flax fibres	0.20	0.29	—	—	0.20	22	0.09
" " " " " "	0.10	0.22	0.22	1.00	0.12	24	0.10
Nettle fibres	0.20	0.41	0.33	1.24	0.16	6.4	0.25
Ramie fibres	0.20	0.27	0.28	0.96	0.09	5.0	0.18
Holocellulose from spruce . . .	0.20	0.93	0.78	1.19	0.21	2.9	0.72
α -cellulose from holocellulose .	0.20	0.51	0.51	1.00	0.19	5.9	0.32
Sulphate cellulose	0.49	0.77	0.82	0.94	0.24	1.9	0.53
" " " " " "	0.19	0.65	0.65	1.00	0.11	2.1	0.54
Sulphite cellulose	0.50	0.77	0.78	0.99	0.35	3.3	0.42
" " " " " "	0.48	0.70	0.74	0.95	0.29	2.9	0.41
" " " " " "	0.20	0.51	0.55	0.93	0.13	3.4	0.38
" " " " " "	0.19	0.55	0.57	0.96	0.10	2.3	0.45
Sulphite cellulose in cuprammonium + 0.1 M NaOH	0.23	0.63	0.64	0.98	0.14	2.5	0.49
" " " " " " + 0.2 M NaOH	0.19	0.54	0.52	1.04	0.13	3.3	0.41
" " " " " " + 0.2 M NaCl	0.20	0.59	0.14	4.2	0	0	0.59
Sulphite cellulose, acetylated .	0.20	0.51	0.55	0.93	0.14	3.8	0.37
Sulphite cellulose, precipitated	0.20	0.88	0.86	1.02	0.22	3.3	0.66
Aged alkali cellulose	0.20	0.89	1.00	0.89	0.05	0.6	0.84
Over-aged alkali cellulose . . .	0.20	1.68	2.19	0.77	0.14	0.9	1.54
" " " " " "	0.20	1.41	1.96	0.72	0.07	0.5	1.34
β cellulose	0.20	2.16	3.08	0.70	0.19	1.0	1.97
BR from sulphite cell. (spruce)	0.21	1.37	1.46	0.94	0.10	0.8	1.27
" " " " " "	0.20	1.04	1.15	0.90	0	0	1.04
BR from sulphate cell. (pine) .	0.22	0.82	1.04	0.79	0.16	2.2	0.66
" " " " " "	0.10	0.58	0.66	0.88	0.04	1.5	0.54

discussed in detail. The diffusion constants are given in units of 10^{-7} cm.²/sec.

The method of calculating D_m and D_A is shown in Fig. 18, where σ^2 and $(A/H)^2$ are plotted against time. Fig. 18 is taken from an experiment with sulphite cellulose (conc. 0.48 %). The points very well fit straight lines, but these lines start at about $t = 2$ days. The first points indicate that the lines should possibly be bent in the beginning (dotted lines). The diffusion process seems to be retarded at first, and not till after some time

does it acquire its real velocity. As this effect is reproducible and has been found in most experiments, it cannot be attributed to any disturbance at the beginning of the experiment. Part of this effect may be attributed to some depolymerization of the cellulose, causing an increase in the diffusion constant (cf. p. 29). It is also possible that the effect may be due to the complexity of the solution. Some of the copper is bound to the cellulose and diffuses as a cellulose-copper complex. Thus the concentration of "low-molecular" copper will be lower in the solution than in the solvent, and this causes osmotic anomalies, until the difference has been neutralized by the diffusion of the copper. In one experiment (sulphite cellulose, $c = 0.20$) ammonia was added to the solvent in sufficient amount to reduce the copper content of the solvent properly, but the effect was observed in the same degree in that experiment. The best method of ensuring equal concentrations of low-molecular material in solvent and solution would have been a dialysis, but no suitable membrane for dialysis has been found.

In those cases where the experiments have been made at different concentrations (unbleached and bleached American linters, flax fibres, sulphate cellulose, sulphite cellulose), the values of k_1 and D_0 agree rather well in the various experiments, which seems to justify the methods of calculation adopted for these quantities.

Fig. 19 shows the calculation of the diffusion of the unbleached American linters at three different concentrations, according to Boltzmann's equation (37). The diffusion constant is given as a function of the concentration along the diffusion curve. The Boltzmann equation has been applied to an average curve, obtained by normal analysis of diffusion curves at different times. It has been noticed that the normal analysis shows no systematic change in the shape of the curve with time, if the zero-point $t = 0$ is taken at the point of intersection in the (t, σ^2) -chart between the time axis and the straight line joining the points from the different exposures (cf. Fig. 18). From Fig. 19 it will be seen that the dependence on concentration is almost linear. At the ends of the curves there are deviations, but these are due to the experimental inaccuracy at the lowest parts of the diffusion curves. The linear extrapolation (dotted line) gives the same value, $D_0 = 0.23$, as the direct calculation with equation (47). The

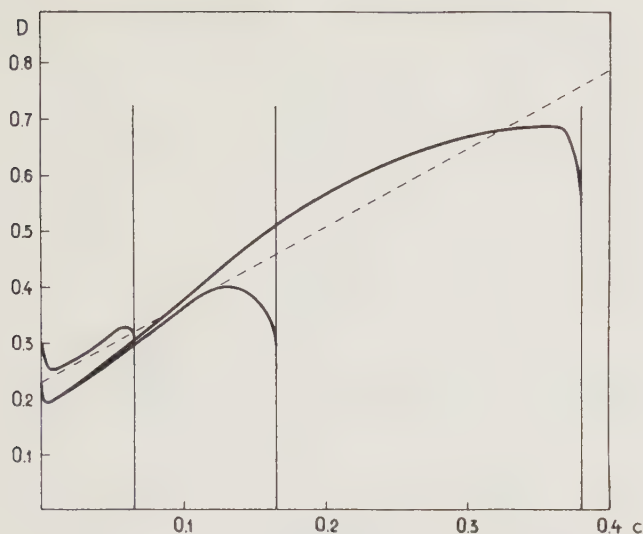


Fig. 19. The diffusion constant of unbleached American linters in cuprammonium as a function of the concentration for three different experiments, calculated according to Boltzmann's equation.

weight average D_m for each experiment agrees very well with the value of D at the middle point of the corresponding line of Fig. 19.

Fig. 20 gives the diffusion curves in normal coordinates for the two experiments with flax fibres. Fig. 21 gives the corresponding Boltzmann calculations. The dots are obtained from the experiment at $c = 0.1$, the circles from that at $c = 0.2$. The dependence on concentration is very high, but the position of the points in the two experiments shows a fairly good correspondence. The linearity is very pronounced. The extrapolation gives $D_0 = 0.10$.

The addition of NaOH to cuprammonium in the experiments with the sulphite cellulose produces no change in the diffusion constant or in the shape of the diffusion curves. This is an indication that any charge effects have already been eliminated by the ions of the cuprammonium, as in the case of sedimentation.

The diffusion with addition of sodium chloride confirms the assumption from the sedimentation analysis that the salt has a salting-out effect. The curve is shown in Fig. 22. The sharp peak in the middle of the curve is caused by a very slowly dif-

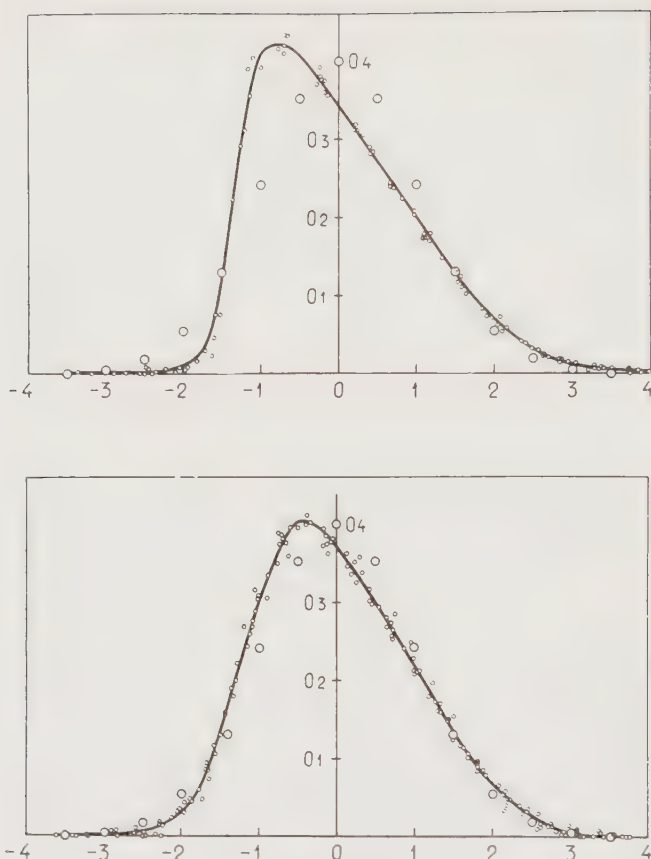


Fig. 20. Diffusion curves (in normal coordinates) of flax fibre cellulose in cuprammonium.

Above: $c = 0.20$, below: $c = 0.10$. The small circles are points obtained from the different exposures, the curves connect the experimental points, and the large circles indicate the corresponding normal curve.

fusing material. It gives rise to the very high value of $D_m/D_A = 4.2$. Part of the cellulose has formed aggregates owing to the addition of the salt, and these aggregates pass into solution without being completely dispersed. They diffuse very slowly. In the sedimentation experiment these aggregates probably sedimented with such rapidity as to elude observation at the ordinary centrifuge velocity. Besides the aggregates, there is ordinarily dispersed cellulose, diffusing faster and giving rise to the spread of the diffusion curve. The experiment is interesting from the

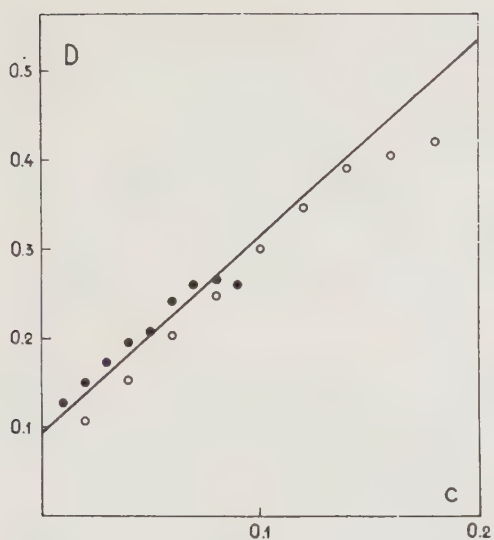


Fig. 21. The diffusion constant of flax fibre cellulose in cuprammonium as a function of the concentration. The dots are points obtained from the experiment at $c = 0.10$, the circles from the experiment at $c = 0.20$.

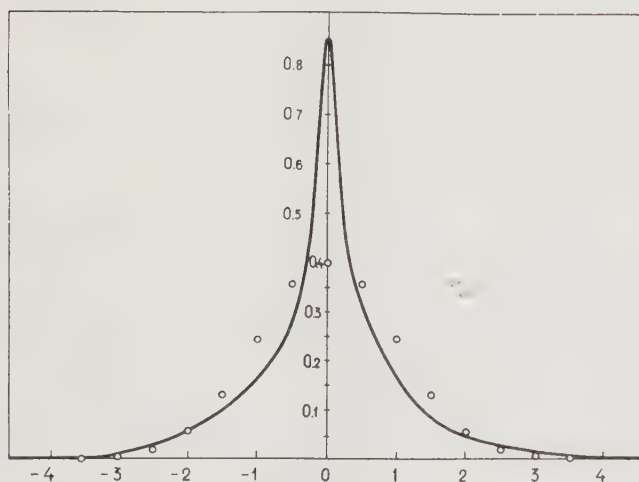


Fig. 22. Diffusion curve (in normal coordinates) of sulphite cellulose in cuprammonium + 0.2 M NaCl.

For explanation see text to Fig. 20.

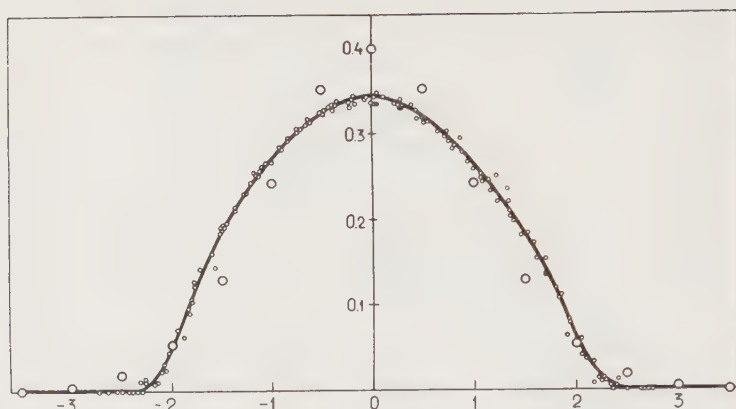


Fig. 23. Diffusion curve (in normal coordinates) of over-aged alkali cellulose. For explanation see text to Fig. 20.

point of view that different methods of calculation could show such marked differences in the results.

From Table 48 it could be seen that the ratio D_m/D_A is frequently less than unity. Fig. 23 shows the diffusion curve of an over-aged alkali cellulose where the effect is most pronounced. The curve deviates considerably from the normal distribution curve. It is compressed at the basis and wider at the top than the corresponding normal curve. The anomaly and shape of the curve does not change with time, according to normal analysis. For that analysis the point $t=0$ is determined from the (t, σ^2) -chart as mentioned on p. 66.

It is very difficult to give any satisfactory explanation of this effect. It might be formally explained by assuming that the diffusion constant depends not only on the concentration but also on the concentration gradient. The shape of the curves indicates a diminution of the diffusion constant at lower gradients. If the molecules become oriented owing to the gradient, this assumption might be justified, but the slow movements of the molecules in the diffusion process could scarcely account for such an orientation if the osmotic forces alone act on the molecules. Mosimann found ([54], p. 66) that cellulose nitrate molecules do not become oriented during sedimentation in high centrifugal fields, and that movement is much more rapid than the Brownian movement in diffusion.

The effect has been found only for cellulose in cuprammonium. It is therefore plausible to assume it to be closely related to the complexity of the solvent and the solution. But obviously the nature of the cellulose also interferes. The effect is very slight for the high-molecular, non-treated celluloses, linters, flax, nettle and ramie fibres. It is most pronounced for the depolymerized celluloses, especially for those regenerated from aged alkali celluloses, also for the rayons. All these no doubt contain oxidized groups. These groups may possibly contribute to the appearance of the effect.

b. The Diffusion of Cellulose Nitrate in Acetone.

The diffusion of cellulose nitrate shows polydispersity and dependence on concentration. The special effect of cellulose in cuprammonium, giving $D_m/D_A < 1$, has not been found with the nitrate. The same methods of calculation have been adopted as for cellulose in cuprammonium. In no case was any delay observed in the starting of the diffusion process. The results are given in the following table.

Table 49. *Diffusion of cellulose nitrate in acetone.*

Nitrate of	Conc.	D_m	D_A	D_m/D_A	$\frac{A M_0}{4 H t}$	k_1	D_0
Unbleached American linters .	0.20	1.42	1.29	1.10	0.42	4.2	1.00
Bleached American linters . .	0.20	1.78	1.65	1.08	0.34	2.4	1.44
Chlorite bleached linters . . .	0.20	1.61	1.49	1.08	0.50	4.5	1.11
Sulphate cellulose	0.20	2.44	2.11	1.15	0.88	5.6	1.56
Sulphite cellulose	0.20	2.38	2.06	1.15	0.82	5.3	1.56
Holocellulose	0.20	3.47	2.70	1.28	0.90	3.5	2.57
α -cellulose from holocellulose .	0.20	2.70	2.25	1.20	0.30	1.3	2.40
Rayon pulp No. 1	0.20	2.64	2.21	1.19	0.70	3.6	1.94
" " No. 2	0.20	2.00	1.80	1.11	0.52	3.5	1.48
" " No. 3	0.20	2.59	2.02	1.28	0.44	2.0	2.15
" " No. 4	0.20	4.41	3.14	1.40	1.40	4.7	3.01
" " No. 5	0.20	2.77	2.17	1.28	0.43	1.8	2.34
" " No. 6	0.20	2.13	2.01	1.06	0.47	2.8	1.66

For discussion of the results the reader is referred to chapter IV.

c. The Diffusion of Sodium Cellulose Xanthate.

The sodium cellulose xanthate solutions undergo spontaneous changes on standing (ripening). These changes proceed more

rapidly at higher temperatures and on dilution. The diffusion experiments must be made in dilute solutions and take considerable time. It is therefore necessary to keep the temperature low. All the experiments were made at 0° , the thermostat being cooled with ice. At this temperature the ripening was very slow and did not disturb the experiments, which had a duration of 2—3 days. In order to keep the thermostat windows free from condensed water, a dry air current was blown against them during the observations. The diffusion constants were transferred to 20° and pure water by ordinary correction formulas.

The charge effects are rather marked in the diffusion as in the sedimentation. They can be lessened and eliminated by the addition of electrolytes, as can be seen from Table 50, showing the results of experiments made with the same viscose at a cellulose concentration of 0.3 %.

Table 50. *Diffusion of xanthate at different electrolyte concentrations.*

M NaOH	M NaCl	D_m
0.26	—	4.14
0.26	0.20	2.54
0.26	0.89	2.01

Some of the xanthates that had been investigated in sedimentation, were also subjected to diffusion experiments in the same electrolyte concentrations as when ultracentrifuged. The following results were obtained.

Table 51. *Diffusion of sodium cellulose xanthates.*

Xanthate	Conc.	D_m	D_A	D_m/D_A	$\frac{A M_0}{4 H t}$	k_1	D_0
Viscose No. 1	0.40	3.62	2.30	1.57	0.27	0.40	3.35
Viscose No. 2	0.40	1.93	1.42	1.36	0.10	0.28	1.83
Xanthate No. 8	0.134	3.40	2.70	1.26	0	0	3.40
Xanthate No. 9	0.134	2.28	1.90	1.20	0	0	2.28
Viscose No. 12	0.20	2.98	1.98	1.50	0	0	2.98
Viscose No. 15	0.20	3.00	2.00	1.50	0.16	0.56	2.84

Some diffusion experiments made at different degrees of ripening indicate that the ripening does not cause any change in the diffusion constant, if sufficient electrolyte is added. The charge

effect is, however, much more marked for a fresh viscose than after ripening for some length of time. As the charge effect is proportional to the concentration, it is shown as a dependence of the diffusion constant on the concentration, i. e. in the form of a skew diffusion curve. Fig. 24 shows the calculation of the diffusion constant, by the Boltzmann equation, from three experiments with the same viscose at different degrees of ripening.

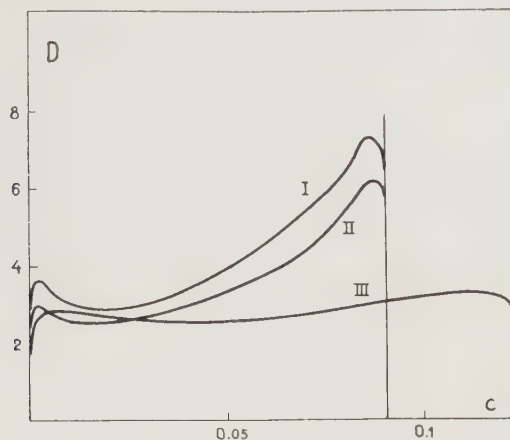


Fig. 24. The diffusion constant of sodium cellulose xanthate (viscose) as a function of the concentration at different degrees of ripening.

- I. Fresh viscose (NaCl-point 7.8 %).
- II. Viscose, suitable for spinning (NaCl-point 4.1 %).
- III. Viscose near coagulation (NaCl-point 0.4 %).

ripening. All the experiments were made with the solvent 0.25 M NaOH + 0.025 M CS₂. It will be seen that the slope dD/dc diminishes on ripening. The extrapolated value, $D_0 = 2.0$, is, however, independent of the ripening. These experiments confirm the generally accepted view regarding the ripening, according to which the chemical process of the ripening is essentially a hydrolysis, the charged xanthate groups being gradually split off from the cellulose.

d. The Diffusion of Sodium Cellulose Glycollate.

Merely a few experiments were made at a glycollate concentration of 0.2 % and different salt concentrations.

Table 52. *Diffusion of sodium cellulose glycollate.*

M NaCl	D_m	D_A	D_m/D_A	$-\frac{AM_0}{4Ht}$	k_1	D_0
0.2	4.22	2.26	1.87	1.14	3.7	3.08
0.5	4.71	3.06	1.54	1.41	4.3	3.30
1.0	3.87	2.25	1.72	0.65	2.0	3.22

The diffusion constants are reduced to pure water.

The charge effect, indicated by the dependence of D on concentration, is rather high, especially at low salt concentrations. The extrapolated value is, however, almost independent of the salt concentration. The charge effect has in all probability been eliminated with 1.0 M NaCl, whence the remaining dependence on concentration must be due to the shape of the glycollate molecules.

Sedimentation Equilibrium.

1. Theory.

If a solution of a high-molecular compound is centrifuged at a constant speed, until equilibrium is established between sedimentation and diffusion in the solution column, the molecular weight can be calculated from the concentration distribution in the cell, according to the formula (Svedberg, [91], p. 8).

$$M = \frac{2 R T \log (c_2/c_1)}{(1 - V\rho) \omega^2 (x_2^2 - x_1^2)}. \quad (48)$$

The concentrations c_1 and c_2 correspond to the distances x_1 and x_2 from the centre of rotation. The other symbols have the previously stated significance (p. 11).

This equation is valid for a monodisperse substance, if the solution obeys the thermodynamic laws of dilute solutions. From the preceding chapters it should be clear that neither of these assumptions holds good for the thread-like cellulose molecules.

The influence of the polydispersity was treated in detail by Lansing and Kraemer [46].

Mosimann [55] found that for cellulose nitrates the equation (48) could be applied only at relatively low concentrations and moderate molecular weights. Otherwise the equation gave too low values of M . Mosimann connected the phenomenon with the swelling pressure of Ostwald (cf. p. 60, equations (36)).

If the dependence of the sedimentation and the diffusion on concentration are expressed by the empiric equations (6) and (41), which have been found to be approximately valid, this will afford a possibility of finding an expression for the sedimentation equilibrium of filamentous molecules. The following reasoning, the

principle of which is taken from Svedberg and Pedersen's monograph [91], p. 8, can be applied.

At equilibrium, sedimentation and diffusion should balance each other. This means that during the time dt the quantity dq of the solute driven by the centrifugal force through the unit surface in the direction of the periphery is equal to that which migrates in the direction of the centre of rotation in virtue of the diffusion.

For the sedimentation we have

$$dq = c \omega^2 x s dt.$$

Applying equation (6) gives

$$dq = c \omega^2 x \frac{s_0}{1 + k c} dt. \quad (49)$$

For the diffusion we have

$$dq = D \frac{dc}{dx} dt$$

and on application of (41)

$$dq = D_0 (1 + k_1 c) \frac{dc}{dx} dt. \quad (50)$$

Equating (49) and (50) and eliminating, we get

$$\frac{dc}{c} = \frac{\omega^2 x s_0}{D_0 (1 + k c) (1 + k_1 c)} dx.$$

Substituting equation (3), which is valid at infinite dilution, gives

$$\frac{dc}{c} = \frac{M(1 - V\rho) \omega^2 x}{R T (1 + k c) (1 + k_1 c)} dx.$$

After integrating this expression between the points x_1 and x_2 , we have for the molecular weight

$$M = \frac{2 R T \cdot \left[\log (c_2/c_1) + (k + k_1) (c_2 - c_1) + \frac{k k_1}{2} (c_2^2 - c_1^2) \right]}{(1 - V\rho) \omega^2 (x_2^2 - x_1^2)} \quad (51)$$

This formula obviously gives a higher M than the original formula (48) because of the terms added to $\log (c_2/c_1)$.

2. Experimental.

a. Sedimentation Equilibrium of Cellulose in Cuprammonium.

The sedimentation equilibrium of cellulose in cuprammonium has been investigated by Kraemer [33, 34, 35, 38]. As Kraemer's experiments were made chiefly with rather low-molecular substances, it was considered to be of interest to extend his measurements to celluloses of higher molecular weights. Merely a couple of experiments of that nature were made, and they gave quite negative results.

The first one was made at a speed of 5 000 r. p. m. (corresponding to a centrifugal force of about 1 400 times gravity) with the sulphite cellulose of Table 12 (p. 36) at the concentrations 0.2 and 0.4 g./100 ml. in the two cells of the rotor. It ran almost for three weeks without the establishment of any equilibrium. A slow sedimentation was observed in one of the cells ($s = 0.9$).

In the second one a slower speed was adopted (1 800 r. p. m., corresponding to a force of about 180 times gravity). The material consisted of sulphite cellulose and sulphate cellulose (p. 36), both in concentrations of 0.2 g./100 ml. No sedimentation at all was observed, and practically no concentration gradient appeared.

Table 53. *Sedimentation equilibrium of aged alkali cellulose in cuprammonium, 0.20 g./100 ml., $dn/dc = 0.00233$, 3 720 r. p. m. Distance from centre of rotation to meniscus 5.49 cm., to cell bottom 6.01 cm. $k = 1.1$, $k_1 = 0.6$.*

r	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
5.49	69	53.8	0.119	98 000	122 000
5.54	73	56.9	0.130	106 000	133 000
5.59	78	60.8	0.143	103 000	132 000
5.64	84	65.4	0.157	93 000	122 000
5.69	91	70.9	0.171	97 000	129 000
5.74	98	76.4	0.187	93 000	129 000
5.79	108	84.1	0.204	94 000	134 000
5.84	118	91.9	0.223	94 000	140 000
5.89	130	101.3	0.244	94 000	143 000
5.94	144	112.2	0.267	93 000	147 000
5.99	159	123.9	0.292	96 000	157 000
6.01	166	129.3	0.303		
M_w				96 000	136 000

Table 54. *Sedimentation equilibrium of BR from sulphate cellulose (pine) in cuprammonium, 0.20 g./100 ml., $dn/dc = 0.00233$, 3 720 r.p.m. Distance from centre of rotation to meniscus 4.67 cm, to cell bottom 5.20 cm. $k = 1.7$, $k_1 = 2.0$.*

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
4.67	74	58.0	0.110	146 000	217 000
4.72	80	62.6	0.123	140 000	217 000
4.77	88	68.9	0.137	142 000	229 000
4.82	95	74.4	0.153	127 000	214 000
4.87	103	80.7	0.169	128 000	225 000
4.92	111	86.9	0.187	127 000	237 000
4.97	119	93.2	0.207	119 000	233 000
5.02	129	101.0	0.228	112 000	235 000
5.07	140	109.6	0.250	115 000	254 000
5.12	151	118.3	0.275	109 000	255 000
5.17	162	126.9	0.301	108 000	271 000
5.20	169	132.3	0.318		
M_w				122 000	238 000

Two experiments were made with celluloses of lower molecular weights (aged alkali cellulose, p. 39, and BR from sulphate cellulose of pine, p. 41). The establishment of equilibrium took about 10 days. The results, showing the molecular weights of the cellulose copper complex anion (cf. p. 89), are given in the Tables 53 and 54.

It will be seen from the tables that the calculation with equation (48) gives a decreasing series through the cell, whereas (51) gives an increasing series, which is natural for a polydisperse material. The weight-average molecular weights from equation (51) are in closer correspondence with the molecular weights from sedimentation and diffusion (Table 68, p. 89), which are 210 000 and 320 000 respectively. Even if the correspondence is not complete, it is obvious that the equation (51) gives an estimate of the effect of the concentration, and the values calculated without taking that effect into account will be far too low.

In view of these experiments there is good reason to presume that the sedimentation equilibrium method cannot be used for determining molecular weights of high-molecular celluloses in cuprammonium. Even with lower molecular weights the swelling effects are appreciable. From this it may be inferred that Kraemer's figures for the molecular weights are too low.

b. Sedimentation Equilibrium of Cellulose Nitrate.

The sedimentation equilibrium of cellulose nitrate in different solvents has been investigated by Mosimann [55]. Also for the cellulose nitrates the swelling effects at high molecular weights are appreciable, and Mosimann did not obtain acceptable results for cellulose nitrates of higher molecular weights than about 100 000.

Table 55. *Sedimentation equilibrium of cellulose nitrate of unbleached American linters in amylacetate, 0.102 g./100 ml., $dn/dc = 0.00085$ (assumed value), 2 400 r. p. m. Distance from centre of rotation to meniscus 4.86 cm., to cell bottom 5.25 cm. $k = 4.2$, $k_1 = 4.2$.*

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
4.86	28	16.2	0.0638	426 000	708 000
4.91	28	16.2	0.0734	362 000	642 000
4.96	28	16.2	0.0829	330 000	615 000
5.01	28	16.2	0.0925	291 000	578 000
5.06	28.5	16.5	0.1021	273 000	575 000
5.11	30	17.4	0.1121	234 000	560 000
5.16	32.5	18.9	0.1228	289 000	648 000
5.21	36	20.9	0.1345	270 000	653 000
5.25	42	24.4	0.1451		
M_w				300 000	618 000

Table 56. *Sedimentation equilibrium of cellulose nitrate of sulphite cellulose in amylacetate, 0.102 g./100 ml., $dn/dc = 0.00085$ (assumed value), 2 400 r. p. m. Distance from centre of rotation to meniscus 5.67 cm., to cell bottom, 6.05 cm. $k = 3.6$, $k_1 = 5.3$.*

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
5.67	22.5	13.0	0.0713	266 000	473 000
5.72	22.5	13.0	0.0789	242 000	452 000
5.77	23	13.3	0.0866	221 000	433 000
5.82	23	13.3	0.0944	206 000	424 000
5.87	24	13.9	0.1024	196 000	428 000
5.92	24.5	14.2	0.1107	187 000	426 000
5.97	26	15.1	0.1193	192 000	459 000
6.02	30	17.4	0.1289	217 000	544 000
6.05	38	22.0	0.1359		
M_w				212 000	454 000

Two experiments with cellulose nitrates of higher molecular weights and amylacetate as a solvent were made by the author. The calculations according to the formulas (48) and (51) are given in the Tables 55 and 56. It has been assumed that the values of k and k_1 are the same in amylacetate as in acetone. This assumption is, of course, somewhat arbitrary, but it has some basis in Mosimann's statement ([54], p. 73) that the intrinsic sedimentation constant of cellulose nitrate is independent of the solvent. The density of amylacetate is 0.873, $V = 0.55$ (Mosimann [54]).

The molecular weights calculated from sedimentation and diffusion of these two cellulose nitrates were 780 000 and 430 000 respectively (Table 69, p. 89). These values are in better correspondence with those calculated from equation (51).

The results from the different parts of the cells form a series with a minimum, whereas the series should naturally be monotonically increasing, owing to the polydispersity. In general, the values of k and k_1 should increase with the molecular weight, and thus with the distance from the meniscus. When k and k_1 , as here, have been taken as constants throughout the cell, the correction terms will be too high near the meniscus and too low near the bottom. This presumably accounts for the effect observed.

Two of Mosimann's experiments ([55], Nos. 22 and 27, pp. 388—389) were recalculated, using equation (51). For the cellulose nitrate in question, $I/6$, the value $k = 1.7$ was derived from the sedimentation velocity reported in Mosimann's earlier publication [54]. At higher concentrations k is lower; at $c = 1.0$, k was found to be $= 0.7$. On comparison with other nitrates of cellulose, a value of $k_1 = 0.8$ was assumed to be correct. The results obtained are shown in the Tables 57 and 58.

By extending the experiments to low concentrations, Mosimann found $M_w = 80\,200$ for this nitrate of cellulose. The assumptions made here for the calculation with formula (51) are somewhat approximative, and the deviations from Mosimann's results are certainly within the possible errors.

The values obtained, both from the author's own experiments and from the recalculation of Mosimann's, render it very probable that the concentration effects involved in sedimentation equilibrium measurements are of the same character and magnitude as those observed in sedimentation and diffusion.

Table 57. *Sedimentation equilibrium of cellulose nitrate I/6 in acetone, Mosimann's experiment No. 22, 0.155 g./100 ml. $k = 1.7$, $k_1 = 0.8$.*

x	M	
	(48)(Mosimann)	(51)
4.70	79 800	90 500
4.75	72 000	89 000
4.80	73 300	88 000
4.85	74 900	90 000
4.90	75 300	94 600
4.95	74 800	96 800
5.00	73 500	100 700
5.05	73 500	106 000
5.10	72 800	114 700
5.15	71 700	114 800
5.20	65 600	113 700
5.25	58 300	
M_w	(69 700)	105 000

Table 58. *Sedimentation equilibrium of cellulose nitrate I/6 in acetone, Mosimann's experiment No. 27, 1.000 g./100 ml. $k = 0.7$, $k_1 = 0.8$.*

x	M	
	(48)(Mosimann)	(51)
5.60	34 100	76 200
5.65	32 000	75 500
5.70	30 400	77 400
5.75	29 500	80 200
5.80	28 300	82 800
5.85	27 100	82 100
5.90	25 900	85 600
5.95	24 800	86 600
6.00	23 600	88 600
6.05	22 400	
M_w	(27 100)	82 500

To calculate M_Z -values from the equilibrium experiments is of little avail, when the swelling effects are so marked as in this case (cf. Mosimann [55], p. 394); minor experimental errors affect the M_Z -values very seriously. No attempt was therefore made to calculate M_Z -values.

c. Sedimentation Equilibrium of Sodium Cellulose Xanthate.

A few experiments were made also with sodium cellulose xanthate. In order to retard the ripening effects during the

Table 59. *Sedimentation equilibrium of viscose No. 12*, 0.20 g. cellulose/100 ml. Distance from centre of rotation to meniscus 4.81 cm., to cell bottom 5.17 cm. $k = 1.0$, $k_1 = 0$.

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
4.81	115	67.1	0.138	77 300	88 400
4.86	121	70.7	0.153	74 100	86 100
4.91	131	76.5	0.168	72 600	85 500
4.96	144	84.1	0.185	71 500	85 400
5.01	158	92.3	0.204	70 900	86 200
5.06	175	102.2	0.224	71 300	88 200
5.11	195	113.9	0.247	71 100	89 500
5.16	218	127.3	0.272	71 800	91 800
5.17	223	130.2	0.277		
M_w				72 400	87 400

Table 60. *Sedimentation equilibrium of viscose No. 12*, 0.10 g. cellulose/100 ml. Distance from centre of rotation to meniscus 5.55 cm., to cell bottom 5.93 cm. $k = 1.0$, $k_1 = 0$.

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
5.55	70	34.4	0.059	82 600	87 600
5.60	80	39.2	0.067	83 500	89 400
5.65	92	45.1	0.075	83 600	90 300
5.70	106	52.0	0.086	85 100	92 800
5.75	125	61.3	0.098	86 900	96 000
5.80	147	72.1	0.112	88 600	99 200
5.85	172	84.4	0.128	88 500	100 700
5.90	201	98.6	0.147	89 900	103 600
5.93	221	108.4	0.160		
M_w				86 400	94 700

rather lengthy time required for the establishment of equilibrium (7—9 days), the runs were made at low temperature (0.5°). At the outset the salt point of the viscose was 6 % NaCl. The solvent was 0.2 M NaOH + 1.0 M NaCl, the density of which is 1.049. The partial specific volume is 0.53 (see p. 87). The refractive index increment was $231 \cdot 10^{-5}$ (cf. p. 88). The speed adopted was 5 000 r. p. m. The results are given in the Tables 59—62.

From sedimentation and diffusion the molecular weights were calculated to be 48 000 for No. 12 and 50 000 for No. 15. The

Table 61. *Sedimentation equilibrium of viscose No. 15*, 0.20 g. cellulose/100 ml. Distance from centre of rotation to meniscus 4.73 cm., to cell bottom 5.17 cm. $k = 0.9$, $k_1 = 0.56$.

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
4.73	103	60.0	0.136	72 300	88 100
4.78	106	61.9	0.149	68 100	84 400
4.83	110	64.3	0.163	63 900	80 700
4.88	114	66.6	0.176	60 900	78 200
4.93	119	69.5	0.191	59 200	77 200
4.98	127	74.3	0.206	58 600	78 000
5.03	138	80.7	0.222	61 400	80 700
5.08	154	90.0	0.240	61 400	85 700
5.13	177	103.6	0.260	63 300	90 600
5.17	198	115.7	0.279		
M_w				62 700	82 600

Table 62. *Sedimentation equilibrium of viscose No. 15*, 0.10 g. cellulose/100 ml. Distance from centre of rotation to meniscus 5.42 cm., to cell bottom 5.93 cm. $k = 0.9$, $k_1 = 0.56$.

x	Z	$\frac{dn}{dx} \cdot 10^5$	c	M	
				(48)	(51)
5.42	70	34.3	0.054	89 900	97 500
5.47	72	35.2	0.061	82 000	90 000
5.52	75	36.9	0.069	76 400	84 700
5.57	79	38.8	0.077	72 200	80 900
5.62	85	41.7	0.085	69 800	79 100
5.67	92	45.2	0.094	68 500	78 800
5.72	103	50.5	0.104	69 200	80 600
5.77	118	57.9	0.116	71 400	84 700
5.82	138	67.6	0.129	74 500	90 000
5.87	163	80.0	0.144	79 200	97 900
5.92	200	98.2	0.163	82 100	103 100
5.93	210	103.0	0.167		
M_w				74 800	87 200

differences between the results from the two methods are considerable. It should be mentioned that the diffusion results involve appreciable corrections for temperature, which are somewhat uncertain. A comparison between the results of equilibrium, calculated according to the equations (48) and (51), shows that the equation (51) gives better correspondence between the results from experiments at different concentrations than does the equation (48).

No M_Z -values were calculated.

Molecular Weights.

1. The Partial Specific Volume Factor.

For the calculation of molecular weights from sedimentation and diffusion experiments, it is necessary to know the partial specific volume of the substance in solution.

The complexity of the solution of cellulose in cuprammonium renders the determination of the partial specific volume of the sedimenting and diffusing substance somewhat indistinct. By the general pycnometric method the partial specific volume of the dissolved cellulose can be determined, though the experimental technique is difficult, owing to the high vapour pressure of the solvent.

In order to prevent evaporation, all vessels (dissolving flasks, pycnometer) were filled with a mixture of ammonia gas and air of the same composition as the vapour over the solvent, before filling in the solution. All transfers were made by pressure with gas of the same composition. An Ostwald pycnometer of about 55 ml. volume was employed. The maximum errors are calculated on the basis of a possible weight difference of 3 mg. due to evaporation. Experience showed that such a difference might occur, even when the minutest care had been taken. The material used was a technical wood sulphite cellulose with an α -content of 91 % (No. 4 of Table 28). The measurements were made at 20°, and the results in Table 63 were obtained.

The weighted average is 0.664, which is within the limits of error for all the experiments.

Stamm [77] found $V = 0.642$ for cellulose in cuprammonium. His low value may possibly be due to the evaporation of ammonia from the solution.

Table 63. *Partial specific volume of cellulose in cuprammonium.*

conc.	V
0.4033	0.677 ± 0.033
0.6025	0.687 ± 0.022
0.7720	0.652 ± 0.017
0.8583	0.673 ± 0.016
0.9977	0.660 ± 0.013
1.0485	0.655 ± 0.013
1.4872	0.661 ± 0.009
1.6458	0.667 ± 0.008

Cellulose and copper form a complex compound in the cuprammonium solution. The composition of this compound is not exactly known, as it has not been found possible to isolate it. The investigations by Hess [21, 22] and Traube [95, 96] have rendered it probable that the cellulose is present in the solution as a complex anion containing copper, the cation being cupritetrammonium, $\text{Cu}(\text{NH}_3)_4^{++}$. Hess concluded from polarimetric measurements that the anion contained one atom Cu per glucose unit (C_6), whereas Traube assumed the proportion 1 Cu:2 C_6 , especially from investigations of cupri-ethylenediamine-cellulose solutions.

In this connection it is of interest to note some observations of the refractive index increment of the cellulose in cuprammonium. By the application of the Lorenz-Lorentz formula for the molecular refraction, an increment $dn/dc = 117 \cdot 10^{-5}$ is calculated for cellulose in cuprammonium. This value was confirmed by measurements in a differential prism. Owing to the high vapour pressure, these measurements are not very accurate: values ranging between 110 and $130 \cdot 10^{-5}$ were obtained.

The refractive index increment can also be measured by integrating the scale line displacement curves from sedimentation and diffusion experiments (see Lamm [43], p. 261). In sedimentation the base line is difficult to determine, but in diffusion it is much more accurate. The results from the diffusion experiments are given in Table 64. Only those experiments in which complete dissolution was certain are reported here.

If the last eight experiments, which are concerned with regenerated celluloses, are excluded, the average will be $233 \cdot 10^{-5}$. This value has been used in sedimentation experiments for de-

Table 64. *Refractive index increment of cellulose in cuprammonium, from diffusion experiments.*

Cellulose	c	$A \cdot 10^4$	$\frac{F}{G a b}$	$\frac{dn}{dc} \cdot 10^5$
Bleached Amer. linters	0.52	181.2	0.0668	233
" " " " " " " " " " " "	0.20	104.0	0.0454	236
" " " " " " " " " " " "	0.10	63.8	0.0361	230
" " " " " " " " " " " "	0.09	56.5	0.0361	227
Chlorite bleached linters	0.20	105.6	0.0454	240
Holocellulose from spruce	0.20	110.6	0.0361	200
α -cellulose from holocellulose	0.20	101.0	0.0454	229
Sulphate cellulose	0.49	229.4	0.0488	228
" " " " " " " " " " " "	0.19	103.9	0.0454	248
Sulphite cellulose	0.50	171.0	0.0668	229
" " " " " " " " " " " "	0.48	164.8	0.0668	230
" " " " " " " " " " " "	0.20	146.5	0.0361	264
" " " " " " " " " " " "	0.19	98.4	0.0454	235
Sulphite cellulose, precipitated	0.20	98.0	0.0488	239
Aged alkali cellulose	0.20	119.7	0.0361	216
Over-aged alkali cellulose	0.20	96.7	0.0454	220
" " " " " " " " " " " "	0.20	113.1	0.0361	204
β -cellulose	0.20	87.0	0.0454	198
BR from sulphite cell. (spruce)	0.21	115.7	0.0361	199
" " " " " " " " " " " "	0.20	95.8	0.0454	218
BR from sulphate cell. (pine)	0.22	101.6	0.0454	210
" " " " " " " " " " " "	0.10	57.0	0.0361	206
Average				$225 \cdot 10^{-5}$

termination of the position of the base line (cf. p. 28) and has proved to be correct.

The value obtained is much higher than that measured in the differential prism. This is obviously due to the fact that in the differential prism only the increment of pure cellulose is measured, whereas in diffusion experiments the whole diffusing complex, including the copper and the cupritetrammonium ion, contributes to the refractive index difference between solvent and solution. From the difference between the results of the two kinds of experiments, it should be possible to find the amount of copper which is bound to the cellulose. Unfortunately, no values of the molecular refraction of copper in complex compounds are available, but approximate estimates indicate that the difference corresponds to about one copper atom per glucose unit complexly bound to the cellulose. This is in agreement with the assumption of Hess [21, 22].

The partial specific volume of cellulose being 0.664, a glucose unit of the cellulose has the volume

$$\frac{0.664 \cdot 162 \cdot 10^{24}}{6.02 \cdot 10^{23}} = 178.7 \text{ \AA}^3.$$

One copper atom fills up a space of about $12 \text{ \AA}^3$ (in metallic copper), whence the copper-cellulose complex anion has a volume of $190.7 \text{ \AA}^3$. Its partial specific volume is

$$\frac{190.7 \cdot 6.02 \cdot 10^{23}}{226 \cdot 10^{24}} = 0.508.$$

The cupritetrammonium ion has not been taken into account in this calculation. As the density of this ion certainly does not differ much from that of the solvent, this approximation involves merely a slight error (Kraemer[36]). The calculation involves many approximations, but seems to be the best obtainable with our present knowledge of the cellulose-copper complex. The density of cuprammonium being 0.943, the factor $1 - V_\rho$ will be = 0.521.

For the cellulose nitrate in acetone the partial specific volume was measured by Scholten [65], and was found to be 0.51. This value was used here for the calculations of molecular weights. We get $1 - V_\rho = 1 - 0.51 \cdot 0.792 = 0.596$.

The partial specific volume of sodium cellulose xanthate was measured on a preparation that had been washed with absolute alcohol immediately after the xanthation and dried in vacuo over P_2O_5 (cf. p. 48). The measurements were made pycnometrically at 20° , and the solvent was 5 % NaOH. The results are given in Table 65.

The value $V = 0.530$ was used for calculations of molecular weights for the sodium cellulose xanthates. As the sedimentation and diffusion measurements were reduced to pure water at 20° , the factor $1 - V_\rho$ will be $1 - 0.530 \cdot 0.9982 = 0.471$.

Also for the xanthate the refractive index increment was determined from diffusion experiments (Table 66).

Table 65. *Partial specific volume of sodium cellulose xanthate.*

Preparation		Analysis	conc.	V
I	15.96 % S, 13.47 % Na		0.476	0.532
			0.765	0.532
			0.972	0.530
			1.145	0.529
			2.028	0.526
			3.162	0.527
			4.239	0.529
II	18.56 % S, 12.81 % Na		0.193	0.526
			0.382	0.531
			0.658	0.533
			Average	0.530

Table 66. *Refractive index increment of sodium cellulose xanthate.*

Viscose No.	<i>c</i> (g. cellulose/100 ml.)	<i>A</i> · 10 ⁴	$\frac{F}{G a b}$	$\frac{dn}{dc} \cdot 10^5$
1	0.40	139.3	0.0635	221
2	0.40	141.2	0.0631	223
12	0.20	111.0	0.0448	249
15	0.20	130.0	0.0356	232
Average				231 · 10 ⁻⁵

The value, in virtue of the xanthate groups, is higher than for pure cellulose.

The following table comprises some of the physical constants of the solutions investigated in this paper.

Table 67.

Solute	Solvent	η_{20°	ϱ_{20°	V	1 - $V\varrho$
Cellulose-copper complex anion	Cuprammonium	0.0135	0.943	0.508	0.521
Cellulose nitrate	Acetone . . .	0.00323	0.792	0.510	0.596
Sodium cellulose xanthate . .	Water	0.01005	0.998	0.530	0.471

2. Molecular Weights from Sedimentation and Diffusion.

The results are given in Tables 68, 69, and 70. They show sedimentation constants and diffusion constants at zero concentration, the molecular weights calculated with Svedberg's formula (3)

and the degrees of polymerization (*D.P.*). Both the molecular weights and the degrees of polymerization are averages, as all celluloses are found to be polydisperse. The base molecular weight for the copper-cellulose complex has been assumed to be 226 (= one glucose anhydride + one copper atom). For the cellulose nitrate it was 291, corresponding to a nitrogen content of 13.8 %. The sodium cellulose xanthate was assumed to have the base

Table 68. *Molecular weights of cellulose in cuprammonium.*

Cellulose	s_0	D_0	$M \cdot 10^{-3}$ cell.-copper complex	<i>D.P.</i>	$M \cdot 10^{-3}$ cellulose	Ref. Tables
Georgia cotton	10.4	0.20	2 400	10 800	1 750	2,48
Unbleached Amer. linters	10.3	0.23	2 100	9 300	1 500	3,48
Bleached Amer. linters	7.2	0.49	690	3 000	490	4,48
Chlorite bleached linters	9.2	0.26	1 700	7 300	1 200	5,48
Flax fibres	17.5	0.10	8 200	36 000	5 900	6,48
Nettle fibres	14.0	0.25	2 600	11 600	1 900	7,48
Ramie fibres	10.8	0.18	2 800	12 400	2 000	8,48
Holocellulose from spruce	7.2	0.72	470	2 100	340	9,48
α -cellulose from holocell.	6.5	0.32	950	4 200	680	10,48
Sulphate cellulose	6.5	0.54	560	2 500	400	11,48
Sulphite cellulose	6.3	0.42	700	3 100	500	12,48
Sulphite cell., acetylated	6.3	0.37	800	3 500	570	14,48
Sulphite cell., precipitated	6.3	0.66	450	2 000	320	14,48
Aged alkali cellulose	3.8	0.84	210	940	150	15,48
Over-aged alkali cellulose	1.9	1.44	62	270	44	16,48
β -cellulose	1.6	1.97	38	170	27	17,48
BR from sulphite cell. (spruce)	2.6	1.16	105	460	75	19,48
BR from sulphate cell. (pine)	4.1	0.60	320	1 400	230	20,48

Table 69. *Molecular weights of cellulose nitrate.*

Nitrate of	s_0	D_0	$M \cdot 10^{-3}$	<i>D.P.</i>	Ref. Tables
Unbleached Amer. linters	19.0	1.00	780	2 700	21,49
Bleached Amer. linters	14.0	1.44	400	1 360	22,49
Chlorite bleached linters	18.5	1.11	680	2 300	23,49
Sulphate cellulose	16.2	1.56	420	1 450	24,49
Sulphite cellulose	16.4	1.56	430	1 470	25,49
Holocellulose from spruce	21.6	2.57	340	1 170	26,49
α -cellulose from holocell.	13.4	2.40	230	780	27,49
Rayon pulp No. 1	16.7	1.94	350	1 200	29,49
„ „ No. 2	18.3	1.48	510	1 700	30,49
„ „ No. 3	15.5	2.15	300	1 010	31,49
„ „ No. 4	17.6	3.01	240	820	32,49
„ „ No. 5	16.8	2.34	290	1 000	33,49
„ „ No. 6	23.3	1.66	570	2 000	34,49

Table 70. *Molecular weights of sodium cellulose xanthate.*

Xanthate		s_0	D_0	$M \cdot 10^{-5}$	$D.P.$	Ref. Tables
Viscose	No. 1	2.3	3.4	35	150	37,51
"	No. 2	4.4	1.8	126	530	38,51
Xanthate	No. 8	2.4	3.4	37	150	40,51
"	No. 9	2.7	2.3	61	250	41,51
Viscose	No. 12	2.8	3.0	48	200	44,51
"	No. 15	2.8	2.8	52	220	45,51

formula $C_6H_9O_4(OH)_{0.23}(OCS_2Na)_{0.77}$, which has the molecular weight 238, and the sodium cellulose glycollate $C_6H_9O_4 \cdot OCH_2 \cdot COONa = 242$.

The sodium cellulose glycollate examined, having $s_0 = 3.4$ and $D_0 = 3.2$ (Tables 47, 52), was calculated to have a molecular weight of 55 000 ($D.P. = 230$), if $V = 0.53$.

3. Viscosity Measurements.

The viscosities of cuprammonium solutions of the celluloses were measured in a nitrogen atmosphere with the complete exclusion of the air. For dissolution, the same dissolver flasks as for the sedimentation and diffusion investigations were employed (see p. 23). The viscometer is shown in Fig. 25. It is similar to that one used by Heuser and Green [25]. The solution is filled

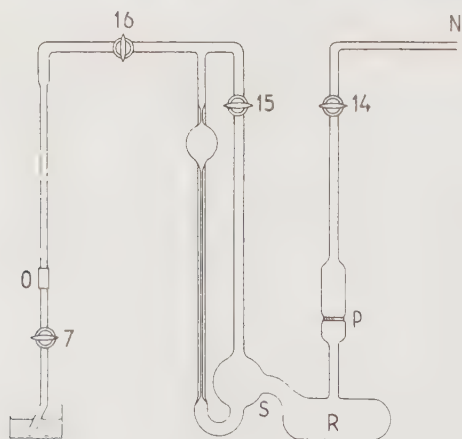


Fig. 25. Viscometer for measurements in a nitrogen atmosphere.

through the cock 14 and the filter *P* (Jena G 2), into the bulb *B*. By tipping the apparatus, the liquid is caused to flow over the threshold *S* and can be pressed up through the capillary into the viscometer bulb. When flowing out through the capillary, the liquid is kept at a constant level by flowing over the threshold *S*. The dimensions of the viscometer were: the bulb volume 2.2 ml., the length of the capillary 14.3 cm. and the radius 0.2322 mm. The water value was 184.0 secs. The Hagenbach correction is very small for these dimensions (Schulz [66]) and has been neglected. The following table gives the results. They have been used for the calculation of degrees of polymerization, according to Staudinger's equation [81, 87]

$$[\eta] = K_m \cdot D.P., \quad (52)$$

where $[\eta]$ is the "intrinsic viscosity" $\lim_{c \rightarrow 0} \left(\frac{\log (\eta/\eta_0)}{c} \right)$, and K_m is a constant. If c is given in grams per 100 ml., the value of K_m is $5 \cdot 10^{-3} = \frac{1}{200}$, according to Staudinger and Daumiller [85].

Kraemer [34, 35, 38] gives $K_m = \frac{1}{260}$.

Table 71. *Viscosity measurements.*

Cellulose	Intrinsic viscosity	<i>D. P.</i> (Staudinger)	<i>D. P.</i> (Kraemer)
Georgia cotton	12.6	2 520	3 270
Unbleached Amer. linters	13.5	2 700	3 510
Bleached Amer. linters	4.6	920	1 200
Chlorite bleached linters	7.7	1 540	2 000
Flax fibres	16.8	3 360	4 360
Nettle fibres	13.5	2 700	3 510
Ramie fibres	10.6	2 120	2 760
Holocellulose from spruce	5.0	1 000	1 300
α -cellulose from holocell.	5.1	1 020	1 330
Sulphate cellulose	4.7	940	1 220
Sulphite cellulose	5.5	1 100	1 430
Sulphite cell., acetylated	5.1	1 020	1 330
Sulphite cell., precipitated	4.5	900	1 170
Aged alkali cellulose	2.3	460	600
Over-aged alkali cellulose	0.6	120	160
β -cellulose	0.20	40	52
BR from sulphite cell. (spruce)	0.95	190	250
BR from sulphate cell. (pine)	2.1	420	550

4. Discussion of the Molecular Weights.

From Table 68 it will be seen that the native celluloses (cotton, bast fibres) have the highest molecular weights. The long-fibred cotton and the linters show great similarity. The bleaching evidently causes some depolymerization; this is the case even with the very mild chlorite bleaching, though merely to a slight extent. The flax fibre contains larger cellulose molecules than any other substance examined.

From the sedimentation experiments with cuprammonium extracts of wood (p. 32), merely rough estimates of the molecular weights can be obtained. On comparison with the values of Table 68, it will be found that the hemicellulose-component may be assumed to have a molecular weight of 50 000—75 000 for the pure carbohydrate, and the cellulose-component about 800 000. As mentioned above (p. 32), only a small part of the cellulose of the wood was dissolved by the cuprammonium-extraction. The dissolved part must be presumed to have been separated from the surface of the wood particles, and it is also fairly obvious that preferably the smallest molecules have been dissolved. For the latter reason it is probable that the average molecular weight of the cellulose in wood is higher than that of the dissolved cellulose.

The isolated wood celluloses have lower molecular weights. The holocellulose contains a rather considerable amount of low-molecular material (see the sedimentation investigation, p. 35). It should be noted that the sedimentation constant relates to the cellulose part of the preparation, whereas the diffusion constant involves also the low-molecular hemicellulose. When the latter is removed by alkali treatment (α -cellulose), the diffusion constant diminishes and the average molecular weight increases. The technical sulphate and sulphite processes yielded celluloses of lower molecular weights than the chlorite decomposition of the wood.

The acetylation of the sulphite cellulose could be carried out without disintegration. It should be mentioned, however, that the acetylation was rather low, and that the acetate was not soluble in any ordinary solvent (p. 38).

The precipitation of the sulphite cellulose from cuprammonium caused some depolymerization.

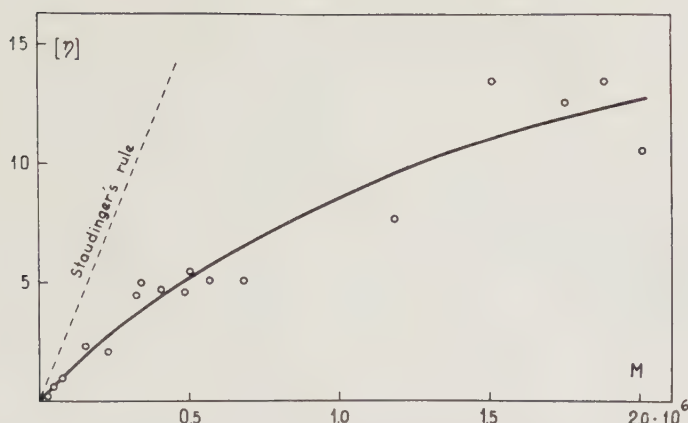


Fig. 26. Relation between molecular weight and intrinsic viscosity for celluloses in cuprammonium.

The latter part of Table 68 shows the alkali celluloses and the regenerated rayon fibres. It will be seen that the molecular size is reduced by alkaline ageing, which is indeed a well-known fact. The alkali-soluble β -cellulose has a very low molecular weight. The two rayon fibres show rather marked differences. The one from sulphate cellulose, which has the best textile properties (Table 18), also has the highest molecular weight.

The figures given here for the molecular weights of cellulose deviate rather considerably from those previously given by Staudinger [84, 87]. This is especially the case as regards cellulose in cuprammonium. A comparison between the Tables 68 and 71 shows that the sedimentation-diffusion method has yielded much higher values for the molecular weights than the viscosity method. It is well known that Staudinger's viscosity rule has been subjected to considerable criticism (cf. the review by Philippoff [60], p. 337 ff., see also Meyer [52]). Fig. 26 shows the relationship between intrinsic viscosity and the molecular weights of cellulose, as obtained by the sedimentation-diffusion method. It will be seen that the relationship is not linear, as Staudinger presumes. The drawn bent line is merely an approximate connection of the points and is not intended to lay down a rule. Generally speaking, the molecular weight increases more rapidly than the viscosity. A similar relation was obtained for the cellulose nitrates by Mosimann [55].

Table 72.

Cellulose	Broken bonds per 10^6 glucose units		
	Cellulose	Nitrate	Difference
Unbleached American linters	110	370	260
Bleached American linters	330	740	410
Chlorite bleached linters	140	440	300
Sulphate cellulose	400	690	290
Sulphite cellulose	320	680	360
Holocellulose from spruce	480	860	380
		Average	330

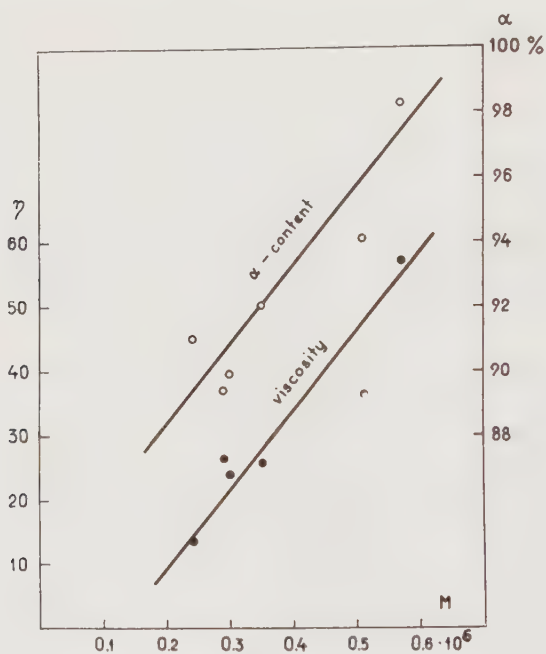


Fig. 27. Relation between molecular weights of cellulose nitrates of rayon pulps and technical properties of the pulps.

The molecular weights obtained are also higher than those reported by Kraemer [33, 34, 35, 38]. His values were obtained by the method of sedimentation equilibrium. As mentioned above (p. 78), the swelling effects in these experiments are rather high, from which it may be inferred that Kraemer's values are too low.

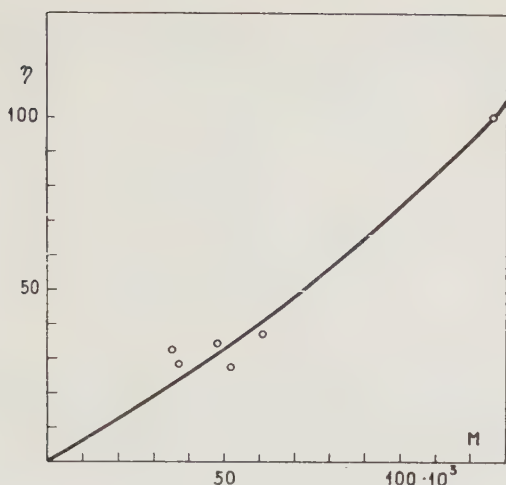


Fig. 28. Relation between molecular weights of sodium cellulose xanthates and technical viscosities of the corresponding viscose.

A comparison between the celluloses and the corresponding nitrates shows that the nitration in all cases has caused decomposition. Table 72 indicates that the depolymerization by this method of nitration is constant, i. e. about the same number of bonds, 0.3 per mille of the existing glucoside bonds, have been broken up by the nitration.

Staudinger's statement [86] that nitration with nitric acid-phosphoric acid could be performed without depolymerization, is thus confuted.

The relation between the technical viscosities and the α -contents of the rayon pulps No. 1—6 (cf. Table 28) and the molecular weights of the corresponding cellulose nitrates is given in Fig. 27. The general tendency towards simultaneous increase is clear.

Also as regards the xanthates a parallelism between technical viscosity (Table 36) and molecular weight can be found (Fig. 28).

5. The Shape of the Cellulose Molecules.

The sedimentation and diffusion methods afford an opportunity for determining the shape of the molecules. As mentioned above (p. 12) the frictional coefficient of the filamentous molecules is

greater than that of a spherical molecule. The frictional ratio, f/f_0 , can be calculated from the formulas

$$f = \frac{R T}{D} = \frac{M(1 - V \varrho)}{s} \quad (53 \text{ a})$$

$$f_0 = 6 \pi \eta N \cdot \left(\frac{3 M V}{4 \pi N} \right)^{1/3} \quad (53 \text{ b})$$

or

$$f/f_0 = \frac{1}{\eta} \cdot \left(\frac{R^2 T^2 (1 - V \varrho)}{162 \pi^2 N^2 D^2 V s} \right)^{1/3} \quad (53 \text{ c})$$

where η is the viscosity of the solvent, and the other symbols have the previously assigned significance.

If the molecule is assumed to be unhydrated and have the shape of an oblong ellipsoid of rotation with the axial ratio $l/d = 1/p$ (l = length, d = diameter), the following equation will be valid

$$f/f_0 = \frac{\sqrt{1 - p^2}}{p^{2/3} \log \left(\frac{1 + \sqrt{1 - p^2}}{p} \right)} \quad (54)$$

(Herzog, Illig and Kudar [20], quoted by Svedberg and Pedersen [91], p. 40 f.). Svedberg and Pedersen give tables for f/f_0 as a function of l/d , but not for $l/d > 100$. For higher values of l/d the equation (54) gives the following figures.

Table 73.

l/d	f/f_0	l/d	f/f_0
100	4.07	600	10.03
150	4.95	700	10.88
200	5.71	800	11.68
300	7.01	900	12.44
400	8.12	1 000	13.16
500	9.12		

The values of l and d are related to the molecular weight and partial specific volume by the equation

$$\frac{\pi l d^2}{6} = \frac{M V}{N} \quad (55)$$

From this equation and the value of l/d , the absolute values of l and d can be calculated. Such calculations have been made for the celluloses and cellulose derivatives investigated here, and the results are given in the following tables.

Table 74. *Molecular shape of cellulose-copper complex in cuprammonium.*

Cellulose	f/f_0	l/d	d	l
			(Ångström units)	
Georgia cotton	9.8	580	18.9	10 700
Unbleached Amer. linters	9.0	490	19.1	9 300
Bleached Amer. linters	6.1	230	16.9	3 900
Chlorite bleached linters	8.6	450	18.1	8 100
Flax fibres	13.1	990	23.6	23 400
Nettle fibres	7.7	360	22.7	8 100
Ramie fibres	10.4	640	19.1	12 300
Holocellulose from spruce	4.7	140	17.6	2 400
α -cellulose from holocellulose	8.4	430	15.3	6 500
Sulphate cellulose	5.9	220	16.1	3 500
Sulphite cellulose	7.1	310	15.5	4 700
Sulphite cellulose, acetylated	7.7	360	15.3	5 500
Sulphite cellulose, precipitated	5.2	170	16.2	2 700
Aged alkali cellulose	5.3	170	12.6	2 200
Over-aged alkali cellulose	4.6	130	9.1	1 200
β -cellulose	4.0	96	8.6	830
BR from sulphite cell. (spruce)	4.8	140	10.6	1 500
BR from sulphate cell. (pine)	6.4	250	12.7	3 200

Table 75. *Molecular shape of cellulose nitrate in acetone.*

Nitrate of	f/f_0	l/d	d	l
			(Ångström units)	
Unbleached Amer. linters	12.2	870	11.3	9 800
Bleached Amer. linters	10.6	670	9.8	6 600
Chlorite bleached linters	11.5	780	11.2	8 800
Sulphate cellulose	9.6	550	10.7	5 900
Sulphite cellulose	9.6	550	10.8	5 900
Holocellulose from spruce	6.3	250	13.1	3 200
α -cellulose from holocellulose	7.7	360	10.1	3 600
Rayon pulp No. 1	8.2	410	11.1	4 600
" " " 2	9.6	550	11.4	6 300
" " " 3	7.9	380	10.8	4 100
" " " 4	6.0	220	12.0	2 700
" " " 5	7.3	320	11.4	3 700
" " " 6	8.2	400	13.2	5 300

Table 76. *Molecular shape of sodium cellulose xanthate.*

Xanthate		ff_0	ld	d	l
				(Ångström units)	
Viscose	No. 1	3.5	71	9.4	670
"	No. 2	4.3	110	12.4	1370
Xanthate	No. 8	3.4	69	9.6	660
"	No. 9	4.3	110	9.7	1070
Viscose	No. 12	3.5	74	10.3	760
"	No. 15	3.7	81	10.2	830
(Sodium cellulose glycollate		3.2	59	11.2	660

It should be pointed out that the assumptions on which these calculations are based are not absolutely valid. The cellulose molecules are not perfect rotational ellipsoids, and they are certainly solvated to some extent. The figures obtained therefore cannot be taken for granted as absolute values. The polydispersity of the celluloses should also be kept in mind. The values are nevertheless of comparative interest.

It is of particular interest to consider the values of d . According to Meyer's model (p. 8) the cross-sectional area of the cellulose molecule is about 33 Å^2 (the dimensions are about $4 \times 8 \text{ Å}^2$). All the values of d obtained indicate a larger cross section, but not to such an extent that the molecule might be considered to consist of a bundle of several parallel chains of glucose units or to be branched. The values of d are thus indicative of the chain-like shape of the cellulose molecule. This chain is not quite extended, but folded or at any rate undulated. When applying the formula (54), valid for ellipsoids, to such a molecular structure, it must give a value of d higher than the width of the chain.

For the celluloses in cuprammonium the values of d vary considerably with the molecular weight. Most of the native celluloses have a d between 15 and 19 Å. There is a slight increase with increasing molecular weight. A larger molecule tends to range itself in a larger number of curves, takes up a wider space, and the use of equation (54) gives a larger cross section. The flax and nettle fibres have a higher d , 23 Å, indicating a more marked folding of the molecules. The low-molecular alkali celluloses and regenerated celluloses (the last five ones in Table 74)

have a more extended shape, d being about $10 \text{ \AA}$. Fig. 29 gives the relation between d and the molecular weight. The points deviate somewhat from a smooth curve. Some of the celluloses are certainly not quite regular in constitution, but contain minute amounts of oxidized groups or other "errors" in the constitution. Such anomalies of the cellulose chains cause changes in the molecular shape, as a rule sharper bendings of the molecules, i. e. higher values of d . This fact will probably explain the

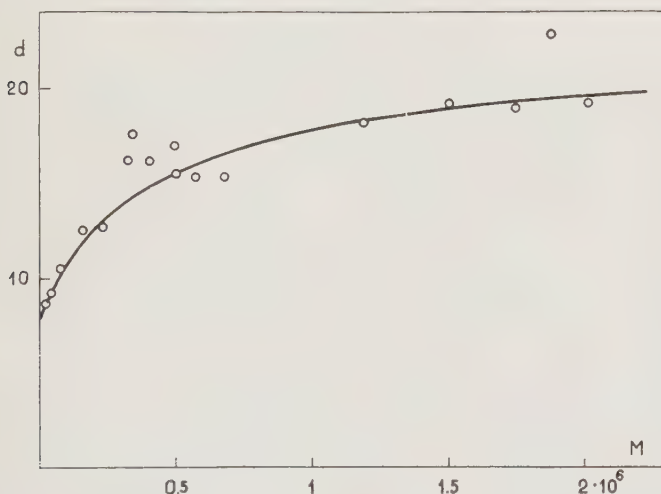


Fig. 29. Relation between molecular weight and the calculated diameter of the molecules of celluloses in cuprammonium.

spread of the points in Fig. 29. The extrapolation of the curve to $M=0$ gives a value of d in approximate correspondence with the X-ray data for the cellulose molecule.

For the cellulose nitrates d is very constant. It should be noted that d is lower for the nitrates than for the corresponding celluloses. When the nitrate groups are attached to the cellulose molecule, it will be elongated by stretching. The nitrate groups have a marked dipole character and a large volume, and both these features preclude a sharper bending between the glucose units.

The sodium cellulose xanthate and glycollate molecules have a shape very similar to that of the most low-molecular celluloses in cuprammonium, d being about $10 \text{ \AA}$. Also for the xanthates, the larger number of undulations (increasing width) with increasing molecular weight is noticeable.

The dependence of the sedimentation constants and the diffusion constants of cellulose and cellulose derivatives, as expressed by the constants k and k_1 of the equations (6) and (41), is certainly a function of the molecular size and shape. It can be observed that, for a given molecular species, the values of k and k_1 are often almost equal. In general, k and k_1 are approximately proportional to the weights or to the lengths of the molecules.

6. The Polydispersity.

It is obvious from the sedimentation and diffusion experiments reported here that all the celluloses investigated are polydisperse, i. e. contain molecules of different sizes. As measures of the polydispersity the quantities $\left(\frac{d B}{d x}\right)_{c=0}$ (p. 18) and D_m/D_A (p. 59) have been given. On the assumption of logarithmic distribution functions, the quantities γ_s (p. 20) and γ_D (p. 59) may be substituted for $\left(\frac{d B}{d x}\right)_0$ and D_m/D_A . They are referred to sedimentation constants and diffusion constants respectively.

It would be of greater interest to have the measures of polydispersity referred to the molecular weights, as in the case of Lansing and Kraemer's "non-uniformity coefficient" β (p. 17). It would be possible to refer γ_s to molecular weights if we knew the relation between molecular weights and sedimentation constants, and correspondingly for γ_D and diffusion constants. However, if the molecules are of various shapes, the molecular weight may vary for a single value of the sedimentation constant or diffusion constant, and no exact relation can be given. Any attempts to give a relation between the polydispersity measured from sedimentation or diffusion experiments and the actual polydispersity of the molecules will therefore yield merely approximate results.

For spherical particles the equation

$$M = \frac{\text{const.}}{D^3} \quad (56)$$

is theoretically valid, because D is inversely proportional to the particle radius. Equation (56) is valid also for the more general

case that f/f_0 is a constant. This rule is easily derived by combining the equations (53 a) and (53 b). From the preceding section it should be clear that f/f_0 varies with the molecular weight, whence the relation (56) could not be used for our purposes.

The other extreme would be the linear, quite extended chain-molecule. In that case l/d would be proportional to the molecular weight. The rotational ellipsoids, assumed for the formula (54), do not differ much from cylinders for large values of l/d . Combining the equations (53 a), (53 b) and (54) gives

$$\frac{1}{D \cdot M^{1/3}} = \text{const.} \cdot \frac{\sqrt{1-p^2}}{p^{2/3} \log \left(\frac{1 + \sqrt{1-p^2}}{p} \right)}$$

and for $M = \text{const.} \cdot \frac{1}{p}$ we get

$$\frac{1}{D} = \text{const.} \cdot \frac{\sqrt{1-p^2}}{p \cdot \log \left(\frac{1 + \sqrt{1-p^2}}{p} \right)}$$

and if the molecules become very long, i. e. $p \rightarrow 0$, we get

$$\frac{1}{D} = \frac{\text{const.}}{p}$$

or

$$M = \frac{\text{const.}}{D} \quad (57)$$

A comparison with Svedberg's formula (3), which could be written

$$M = \text{const.} \cdot \frac{s}{D} \quad (58)$$

shows that for this special case s should be independent of the molecular weight. This extreme case, which was presumed by Kuhn and Kuhn [40] to be valid for "völlig bespülte" filamentous molecules, is never realized, but from Tables 68—70 it should be clear that s varies but slightly as regards the cellulose molecules.

From the equations (56) and (57), representing the extremes, it is plausible to assume a more general equation

$$M = \frac{\text{const.}}{D^a} \quad (59)$$

where a is a constant with a value between 1 and 3. If a similar equation is assumed for the sedimentation constant

$$M = \text{const.} \cdot s^b \quad (60)$$

and equation (58) is taken into account, we get

$$s \cdot D^{a-1} = \text{const.}, \text{ and } D \cdot s^{b-1} = \text{const.}$$

These equations can be simultaneously valid only if

$$(a - 1)(b - 1) = 1. \quad (61)$$

If the logarithmic distribution functions (18), (21) and (33) are valid for the molecular weights, sedimentation constants and diffusion constants, then the equations (59) and (60) can also be applied, and we get the following simple relations between the "non-uniformity coefficients":

$$\gamma_s = \frac{\beta}{b}; \quad \gamma_D = \frac{\beta}{a}. \quad (62)$$

The experimental examination of the validity of the equations (59) and (60) can be made by plotting $\log s$ and $\log D$ in a chart as ordinates against $\log M$. This has been done for the celluloses in cuprammonium in Fig. 30, for the cellulose nitrates

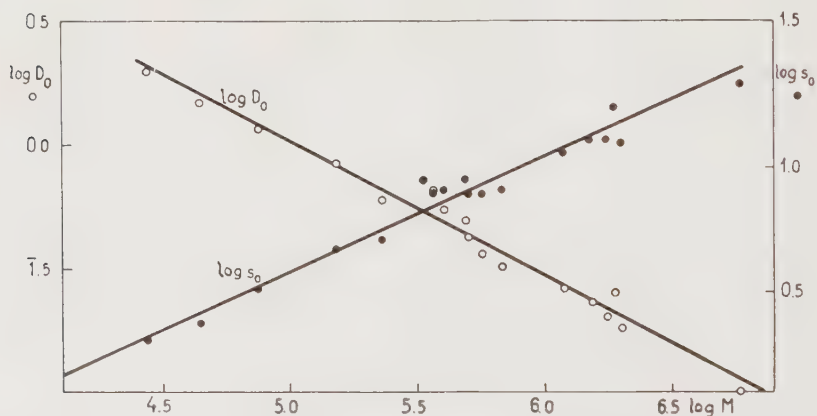


Fig. 30. $\log_{10} s_0$ and $\log_{10} D_0$ as functions of $\log_{10} M$ for celluloses in cuprammonium.

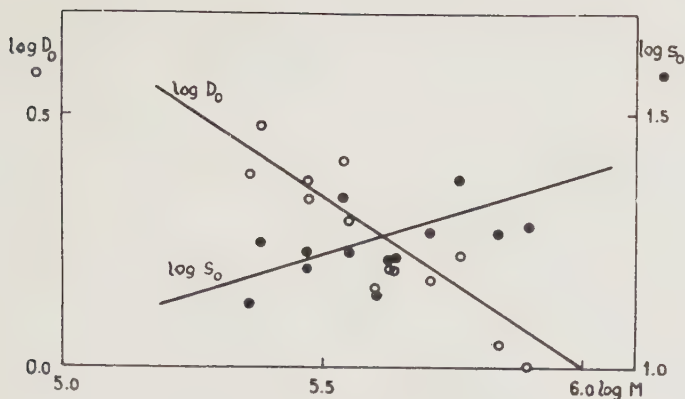


Fig. 31. $\log_{10} s_0$ and $\log_{10} D_0$ as functions of $\log_{10} M$ for cellulose nitrates in acetone.

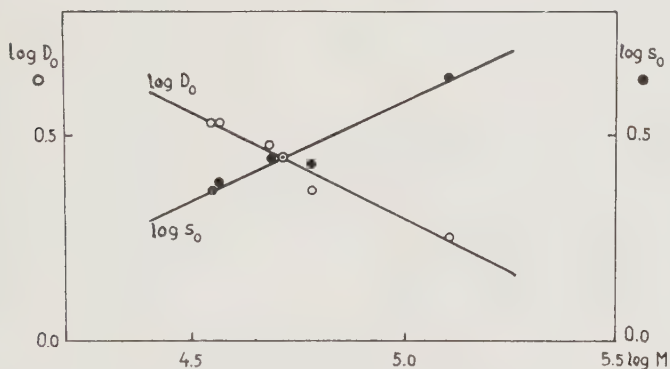


Fig. 32. $\log_{10} s_0$ and $\log_{10} D_0$ as functions of $\log_{10} M$ for sodium cellulose xanthates.

in acetone in Fig. 31, and for the sodium cellulose xanthates in Fig. 32. It is obvious that the points tend to range themselves in straight lines; this tendency is rather marked as regards the celluloses and xanthates, less so for the nitrates, though evident even there. The straight lines drawn in the diagrams are fitted to the points by the method of least squares (for the cellulose nitrates the points from the cotton celluloses are not taken into consideration). From the slope of the lines the values of a and b given in Table 77 are obtained.

The condition (61) is well fulfilled. The value of a is lower for the cellulose nitrates than for the celluloses in cuprammo-

Table 77. *The constants a and b of the equations (59) and (60).*

	a	b	$(a-1)(b-1)$
Cellulose in cuprammonium	1.83	2.21	1.00
Cellulose nitrate in acetone	1.46	3.17	1.00
Sodium cellulose xanthate	1.92	2.07	0.98

Table 78. *Non-uniformity coefficients.*

a) Cellulose in cuprammonium.

Cellulose	γ_s	β
Georgia Cotton	0.31	0.68
Unbleached American linters	0.20	0.44
Bleached American linters	0.48	1.06
Chlorite bleached linters	0.47	1.04
Flax fibres	0.33	0.73
Nettle fibres	0.30	0.66
Ramie fibres	0.39	0.86
Holocellulose from spruce (cellulose part)	0.62	1.37
α -cellulose from holocellulose	0.66	1.46
Sulphate cellulose	0.48	1.06
Sulphite cellulose	0.54	1.19
Aged alkali cellulose	0.72	1.59
Over-aged alkali cellulose	0.88	1.94
BR from sulphite cellulose (spruce)	0.71	1.57
BR from sulphate cellulose (pine)	0.56	1.24

b) Cellulose nitrate in acetone.

Nitrate of	γ_s	γ_D	β	
			from sed.	from diff.
Unbleached American linters	0.12	0.50	0.38	0.73
Bleached American linters	0.15	0.45	0.48	0.66
Chlorite bleached linters	0.22	0.45	0.70	0.66
Sulphate cellulose	0.26	0.61	0.82	0.89
Sulphite cellulose	0.33	0.61	1.05	0.89
Holocellulose from spruce	(0.54)	0.81	1.71	1.18
α -cellulose from holocellulose	0.67	0.70	2.12	1.02
Rayon pulp No. 1	0.42	0.68	1.33	0.99
" " No. 2	0.40	0.53	1.27	0.77
" " No. 3	0.55	0.81	1.74	1.18
" " No. 4	0.53	0.95	1.68	1.39
" " No. 5	0.53	0.81	1.68	1.18
" " No. 6	0.33	0.39	1.05	0.57

c) Sodium cellulose xanthate.

Xanthate		γ_s	γ_D	β	
				from sed.	from diff.
Viscose	No. 1	0.45	1.10	0.93	2.1
"	No. 2	0.54	0.91	1.12	1.75
"	No. 3	0.32	—	0.66	—
Xanthate	No. 8	0.49	0.78	1.02	1.50
"	No. 9	0.40	0.69	0.83	1.33
"	No. 10	0.54	—	1.12	—
"	No. 11	0.42	—	0.87	—
Viscose	No. 12	0.57	1.04	1.18	2.0
"	No. 15	0.48	1.04	1.00	2.0

nium. This is in accordance with the fact that the cellulose nitrates have a more elongated shape than the corresponding celluloses (cf. p. 99).

The Tables 78 show the calculations of β by use of the equations (62) and the values of a and b from Table 77. As mentioned above (p. 64), the diffusion measurements of cellulose in cuprammonium cannot be used for polydispersity determinations, owing to other, uncontrollable effects.

The experimental errors and the approximations involved render the results rather inaccurate. Some conclusions, however, can certainly be drawn.

There is a general tendency towards increase in the polydispersity with decreasing molecular weight. The lowest polydispersity is found with the native fibre celluloses. Bleaching of the linters increases the coefficient β . The celluloses isolated from wood are still more polydisperse, and especially the alkaline depolymerization involved in the viscose process increases the polydispersity.

The cellulose nitrates show a somewhat lower β than the corresponding celluloses, despite their lesser molecular weight. If this difference is of any significance it should mean that the nitration attacks preferably the largest molecules and reduces their chain length.

In the case of the cellulose nitrates and the xanthates the possibility is afforded of calculating β from both sedimentation and diffusion. The results from the two methods show considerable differences. These may presumably be attributed to failures

of the assumed logarithmic distribution functions. If the results agree (as in the case of the nitrates of chlorite bleached linters and sulphate cellulose) it may be concluded that the assumed distribution is a fairly good approximation to the true distribution.

Even if the agreement is not complete, it is obvious that the sedimentation and diffusion data yield comparable results for the polydispersity. The correlation coefficients between γ_s and γ_D are 0.78 and 0.53 for the cellulose nitrates and the sodium cellulose xanthates respectively.

Summary.

The purpose of this work has been to give a survey of the sedimentation and diffusion behaviour of cellulose and some of its derivatives.

1. It has been found that the dependence of the sedimentation velocity of filamentous molecules on the concentration of the solution can approximately be expressed by the equation

$$s = \frac{s_0}{1 + k'c},$$

where k is a constant and s_0 is the sedimentation constant at infinite dilution. The shape of the sedimentation curve at different concentrations has been discussed in view of this relation.

2. Setting out from the fact that molecules of different sizes sediment at different rates, it has been shown that the width of the sedimentation curve may be taken as a measure of the polydispersity of the material. It is proposed to use the quantity

$\left(\frac{dB}{dx}\right)_{c=0}$, where B is the curve width and x is the distance in the sedimentation direction, as a measure of the polydispersity with regard to sedimentation.

3. Sedimentation and diffusion experiments have been made with the following solutions: cellulose in cuprammonium, cellulose nitrate in acetone, sodium cellulose xanthate in alkaline aqueous solutions, and sodium cellulose glycollate in water.

4. Special arrangements for the manipulation in nitrogen atmosphere with cuprammonium solutions have been described.

5. The investigated celluloses were firstly native fibre celluloses, and secondly wood celluloses. Their isolation and preparation as well as the method of nitration (in a mixture of nitric acid, phosphoric acid and phosphorous pentoxide) have been described.

6. A method for the determination of polydispersity from diffusion measurements has been suggested, the ratio D_m/D_A being proposed as a measure of the polydispersity with regard to diffusion.

7. The skewness of diffusion curves has been discussed, and a simple formula is given for determining the dependence of the diffusion constant on the concentration from the skewness of the curves, assuming a linear dependence on concentration, $D = D_0(1 + k_1 c)$.

8. For celluloses in cuprammonium it has been found that the diffusion process frequently seems to be at first retarded and does not acquire its real velocity until after the lapse of some time.

9. The diffusion of cellulose nitrate, sodium cellulose xanthate and sodium cellulose glycollate has been found to proceed more normally.

10. It has been shown that the dependence of sedimentation and diffusion on the concentration also affects the sedimentation equilibrium of filamentous molecules. A formula has been derived for the calculation of sedimentation equilibrium in such cases. It gives higher values for the molecular weights than the ordinary formula. By experiments with cellulose in cuprammonium, cellulose nitrate in amylacetate and sodium cellulose xanthate in aqueous solutions, the derived formula has been proved to give reasonable results.

11. The partial specific volume of cellulose in cuprammonium was found to be 0.664. From refractometric measurements it has been inferred that the cellulose-copper complex anion contains one copper atom per glucose unit, and its specific volume was found to be 0.508. The partial specific volume of sodium cellulose xanthate was found to be 0.530.

12. The molecular weights of the investigated celluloses and cellulose derivatives have been determined by sedimentation and diffusion measurements. The native fibre celluloses were found to have higher molecular weights ($1.5 - 2 \cdot 10^6$) than the chemically isolated wood celluloses ($0.34 - 0.68 \cdot 10^6$). The highest molecular weight was found for the cellulose from flax fibres ($5.9 \cdot 10^6$). The alkali treatment involved in the viscose process entails depolymerization.

13. From attempts to extract the cellulose of wood directly

with cuprammonium it is inferred that the average molecular weight of cellulose in wood is at least 800 000. The chemical bonds between lignin and the carbohydrates of wood are more readily hydrolyzed than the glucosidic bonds in the cellulose chains, though there is but little difference.

14. By comparison with viscosity measurements on celluloses in cuprammonium it has been shown that the results from sedimentation and diffusion are not in agreement with Staudinger's viscosity rule. The molecular weight increases more rapidly than the viscosity. Even for low molecular weights the sedimentation-diffusion method gives appreciably higher molecular weights than does Staudinger's viscosity rule.

15. Nitration in a mixture of nitric acid and phosphoric acid entails disintegration of the cellulose molecules. About 0.3 per mille of the glucose bonds are ruptured by the nitration process applied.

16. The sodium cellulose xanthates and the sodium cellulose glycollate have relatively low molecular weights, about 50 000.

17. The shape of the molecules has been determined by sedimentation and diffusion experiments. The molecules of cellulose and cellulose derivatives are filamentous, and consist of simple glucose chains without branching. The results indicate that the molecules are slightly folded or undulated.

18. The cellulose nitrate molecules have a more extended shape than the corresponding cellulose molecules, presumably owing to the dipole character and large volume of the nitrate groups, which preclude bending.

19. The methods of measuring polydispersity by sedimentation and diffusion experiments, and the possibility of relating the different measures to each other and to Lansing and Kraemer's "non-uniformity coefficient" β have been discussed. On the assumption of logarithmic distribution functions, simple expressions for the relations have been derived.

20. There is a general tendency towards increase in the polydispersity with decreasing molecular weight. The celluloses isolated from wood are more polydisperse than the native fibre celluloses. The alkaline depolymerization involved in the viscose process increases the polydispersity.

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